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Lithological and Geochemical Responses to Abrupt Global and Regional Paleoenvironmental Changes During the Aptian in a Hemipelagic Setting of the Eastern Iberian Peninsula: A Multi-Proxy Approach

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

LITHOLOGICAL AND GEOCHEMICAL RESPONSES TO ABRUPT GLOBAL AND
REGIONAL PALEOENVIRONMENTAL CHANGES DURING THE APTIAN IN A
HEMIPELAGIC SETTING OF THE EASTERN IBERIAN PENINSULA: A MULTI-
PROXY APPROACH

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

EARTH SYSTEMS SCIENCE

by

Jander Socorro

2020

To: Dean Michael R. Heithaus
College of Arts, Sciences and Education

This dissertation, written by Jander Socorro, and entitled, Lithological and Geochemical Responses to Abrupt Global and Regional Paleoenvironmental Changes during the Aptian in a Hemipelagic Setting of the Eastern Iberian Peninsula: A Multi-Proxy Approach, having been approved in respect to style and intellectual content is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Date of Defense: March 18, 2020

The dissertation of Jander Socorro is approved.

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Vice President for Research and Economic Development
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Florida International University, 2020

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DEDICATION

I dedicate this dissertation to my parents. This work would not have been possible without their support, understanding and encouragement.

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ABSTRACT OF THE DISSERTATION

LITHOLOGICAL AND GEOCHEMICAL RESPONSES TO ABRUPT GLOBAL AND
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PROXY APPROACH

by

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Miami, Florida

Professor Florentin Maurrasse, Major Professor

Intense episodes of environmental perturbations and regionally to globally distributed, oxygen-deprived marine facies characterize the Cretaceous sedimentary record. The Organyà Basin in the Spanish Pyrenees chronicles this period in expanded stratigraphic sequences that enabled high-resolution sampling and detailed analysis of disturbances poorly recorded in more lithologically condensed sections. Here, I present an integrated multi-proxy study aimed at understanding the Basin's response to changing paleoenvironmental conditions during the early Aptian stage of the Cretaceous.

Results from the El Pui section indicate that large-scale ($> 1\text{‰}$), negative carbon isotope excursions (CIEs) that show no corresponding shifts in local sources of organic matter (OM) and are simultaneously recorded at coeval localities result from the increased input of isotopically light carbon into the oceanic/atmospheric system, altering the isotopic ratio ($\delta^{13}\text{C}$) of the global carbon reservoir. The El Pujal section, in continuation with the series previously recorded at El Pui, registers a $\delta^{13}\text{C}_{\text{org}}$ curve that is

consistent with the pattern reported for carbon isotope segment C5 within Oceanic Anoxic Event 1a (OAE1a). Pulses of fluvial fluxes associated with climatic fluctuations explain the alternating lithology, with limestones representing the least terrestrially influenced end-member and marlstones representing episodes of highest terrigenous influence. Primary production sustained by fluvial inputs of biolimiting elements provided abundant labile OM conducive to oxygen-deprived conditions, as attested by concomitant peaks in total organic carbon (TOC), relatively lower benthic faunal counts, lower bioturbation index, higher concentration of pyrite and peaks in redox-sensitive trace elements. However, OM preservation was not chiefly controlled by redox conditions as physical encapsulation by clay minerals and coincident inputs of terrestrial OM with more recalcitrant properties likely played a significant role. A demise of previous conditions is registered in the uppermost portion with hard limestone low in TOC, and major elements and with lower ratios of autochthonous to allochthonous OM, indicating a reduction in fluvial fluxes and surface-water fertility suggesting dryer climatic conditions. Changes in microfacies, with coarser grain packstones, fewer planktonic foraminifera and an increase in benthic taxa, imply a shallowing of the basin, similar to conditions previously reported in the neighboring Basque-Cantabrian Basin at the end of segment C5.

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ABBREVIATIONS AND ACRONYMS

%	Percent
Σ EIs	Sum of enrichment indices
°	Degrees
°C	Degrees Celsius
μL	Microliter
μm	Micrometers
‰	Per mille
ACL	Average chain length
Al	Aluminum
ASV	Average Shale Value
Au	Gold
BI	Bioturbation index
BOD	Biological oxygen demand
CaCO ₃	Calcium carbonate
CIE	Carbon isotope excursion
cm	Centimeters
cm/kyr	Centimeters per thousand years
cm ²	Centimeters squared
Co	Cobalt
CO ₂	Carbon dioxide
CPI	Carbon preference index
Cr	Chromium

Cu	Copper
DCM	Dichloromethane
DI	Deionized water
DIP	Dissolved inorganic phosphate
DOP	Dissolved organic phosphate
EA-IRMS	Elemental analyzer isotope ratio mass spectrometer
ECS	East China Sea
EI+	Positive mode electron impact ionization
EIs	Enrichment indices
GC-MS	Gas chromatography mass spectrometry
GC-MS/MS	Gas chromatography tandem mass spectrometry
HCl	Hydrochloric acid
hrs	Hours
ICVS	Initial calibration verification standard
K-feldspar	Potassium feldspar
km	Kilometers
Kyr	Thousand years
LA-ICP-MS	Laser ablation-inductively coupled plasma mass spectrometry
LIPs	Large igneous provinces
m	Meters
MeOH	Methanol
mins	Minutes
ml	Milliliters

mm	Millimeter
Mo	Molybdenum
MRM	Multiple reaction monitoring
ms	Millisecond
Mya	Millions of years ago
Myr	Million years
<i>n</i> -alkanes	Normal alkanes
NASC	North American Shale Composite
ng/μL	Nano-grams per microliters
ng/g dw	Nano-grams per gram of dry weight
Ni	Nickel
NIST	National Institute of Standards and Technology
OAE	Oceanic Anoxic Event
OAE1a	Oceanic Anoxic Event 1a
OAE1b	Oceanic Anoxic Event 1b
OAE1c	Oceanic Anoxic Event 1c
OAE1d	Oceanic Anoxic Event 1d
OAE2	Oceanic Anoxic Event 2
OAE3	Oceanic Anoxic Event 3
OBABV	Organya Basin's average background value
OEP	Odd to even preference
OJP	Ontong Java Plateau
OM	Organic matter

OMZ	Oxygen minimum zone
PAAS	Post Archean Australian Shale
PAH	Polycyclic aromatic hydrocarbons
PCA	Principal Component analysis
PETM	Paleocene-Eocene thermal maximum
P-feldspar	Plagioclase feldspar
pH	Negative log of the hydrogen ion concentration
Ph	Phytane
ppm	Parts per million
ppt and ppm*10 ⁻³	Parts per thousand
Pr	Pristane
rpm	Revolutions per minute
RSTEs	Redox sensitive trace elements
SB-V	Songliao Basin
SEM	Scanning electron microscope
Si	Silicon
SIM	Selective ion monitoring
SPCU	South Pyrenean Central Unit
SSTs	Sea surface temperatures
TAR	Terrestrial aquatic ratio
TC	Total carbon
TEX ₈₆	Tetraether index of 86 carbon atoms
Th	Thorium

Ti	Titanium
TIC	Total inorganic carbon
TLE	Total lipid extract
Tm	17 α -22,29,30-trisnorhopane
TOC	Total organic carbon
Ts	18 α -22,29,30-trisnorneohopane
U	Uranium
UCM	Unresolved complex mixture
V	Vanadium
VPDB	Vienna-Pee Dee Belemnite
wt%	Weight percent
XRD	X-ray diffraction
$\delta^{13}\text{C}_{\text{carb}}$	Stable carbon isotopic signature – carbonate fraction
$\delta^{13}\text{C}_{\text{org}}$	Stable carbon isotopic signature – organic fraction

1 INTRODUCTION

The Earth experienced some of the warmest temperatures during the Cretaceous Period. As the greenhouse condition reached its peak during the Cenomanian/Turonian Cretaceous Thermal Maximum, paleo-sea surface temperature (SST) records extracted from planktonic foraminifera ($\delta^{18}\text{O}$) and organic biomarkers (TEX_{86}) show that temperatures in the equatorial Atlantic Ocean were substantially warmer than in the present ($\sim 27\text{-}29^\circ\text{C}$), with average values exceeding 35°C (Forster et al., 2007; O'Brien et al., 2017). The unusually warm global climatic conditions coupled with a shifting paleogeography (Fig. 1-1) are reported to have led to reduced latitudinal temperature gradients, accelerated hydrological cycles, intensified continental weathering and runoff, and fluctuations in eustatic sea level. (Barron, 1983; Haq et al., 1987; Barron et al., 1989; Frakes et al., 1992; Huber et al., 1995, 2018; Tarduno et al., 1998; Weissert et al., 1998; Blättler et al., 2011; Föllmi, 2012; Jenkyns et al., 2012; Haq, 2014; Mutterlose et al., 2014; Lechler, 2015; O'Brien et al., 2017; Charbonnier et al., 2018). These extreme greenhouse conditions have been attributed to elevated concentrations of atmospheric

Figure 1-1 Paleogeographic distribution of major landmasses during the Early Cretaceous ~120 Mya. Figure from <http://cpgeosystems.com/paleomaps.html>.

CO₂ associated with intense tectonic rifting and volcanism, but also to the presence of extensive wetlands that may have provided water vapor as a supplementary greenhouse gas (Arthur et al., 1985; Barron and Washington, 1985; Larson, 1991; Erba and Tremolada, 2004; Weissert and Erba, 2004; Fletcher et al., 2008; Méhay et al., 2009; Wang et al., 2014; Naafs et al., 2016; Hay et al., 2019). Evidence from that time includes remarkably low plant stomatal density, the emplacement of coeval large igneous provinces (LIPs), namely the Ontong Java Plateau (~ 120 and ~ 90 Mya), Kerguelen Plateau (~ 118, ~ 108 and ~ 95 Mya) and Caribbean Plateau (~ 94 – 87 Mya), and characteristic negative excursions in the carbon isotopic record ($\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$) (Fig. 1-2) (Tarduno et al., 1991; Erbacher et al., 1996; Bralower et al., 1999; Larson and Erba, 1999; Leckie et al., 2002; Haworth et al., 2005; Tejada et al., 2009; Sun et al 2016; Charbonnier and Föllmi, 2017). While volcanogenic sourced CO₂ is relatively depleted in $\delta^{13}\text{C}$ (~ -5‰) it is argued that such release is insufficient to produce the drastic negative shifts recorded in the global carbon isotope values (>3‰) (van Breugel et al., 2007). Therefore, dissociation of methane hydrates with much lighter $\delta^{13}\text{C}$ values (~ -60‰) (Kvenvolden, 1993) has been proposed as a possible causal factor of the large negative inflections recorded throughout the Cretaceous (Jahren et al., 2001; 2005; Beerling et al., 2006; van Breugel et al., 2007).

Most remarkably, these negative carbon isotope excursions are followed by pronounced positive spikes (Fig. 1-2), spanning ~ 500 kyr – 1 Myr in marine carbonates ($\delta^{13}\text{C}_{\text{carb}}$) and both marine and non-marine organic matter (OM) ($\delta^{13}\text{C}_{\text{org}}$) (Arthur et al., 1988; 1990; Weissert, 1989; Erba, 1994; Erbacher et al., 1996; Hasegawa, 1997; Menegatti et al., 1998; Bralower et al., 1999; Larson and Erba, 1999; Leckie et al., 2002;

Figure 1-2 The mid-Cretaceous record of major black shale deposition associated with oceanic anoxic events (OAEs) in the context of time, emplacement of LIPs, strontium isotope record, the carbon isotope record and eustatic sea level fluctuations. Notice the negative inflections that precede most of the major OAEs in relation to the timing of LIPs. Subsequent positive shifts coincide with the widespread deposition of OM-rich marine sediments. Figure from Leckie et al. (2002) and data from Bralower et al. (1997, 1999), Erbacher et al. (1996) and Haq et al. (1988).

Weissert and Erba, 2004; Jenkyns, 2010). These positive carbon isotopic excursions (CIEs) reveal periods of enhanced OM sequestration, because photosynthetic organisms preferentially take up the lighter form of carbon (^{12}C) and the carbon isotopes are fractionated, leaving the remaining global carbon reservoir enriched in ^{13}C (Arthur et al., 1988; van Bentum et al., 2012). In addition, positive carbon isotopic excursions are associated with increased marine productivity, enhanced preservation of OM, and

appreciable changes in the marine microfauna and nannoflora (Erba, 1994; Jenkyns, 2010; Föllmi, 2012). These changes thus indicate significant perturbation of the global carbon cycle that affected the carbon isotope composition of exchangeable carbon in the global reservoir. Because every reservoir of carbon, whether oceanic, terrestrial or atmospheric, reflects the global isotopic signature, even if it is not directly sequestering carbon, the carbon isotopic pattern can thus serve as an important global correlation tool. The applicability of using stable carbon isotope for global correlation was discussed by Scholle and Arthur (1980), and further supported by subsequent works (Weissert and Bréhéret, 1991; Erbacher et al., 1996; Menegatti et al., 1998, and others). Menegatti et al. (1998) subdivided the carbon isotope curve for the late Barremian and Aptian stages into segments (C1-C8), based on the similar pattern observed in the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ record of two Alpine Tethys sections (Roter Sattel, Switzerland; Cismon, Italy). Later, Bralower et al. (1999) expanded the carbon isotope segments into the Albian stage using several stratigraphic sections from Mexico. Since then, the stable carbon isotope curve has been calibrated with biostratigraphy and magnetostratigraphy and is becoming one of the main correlation tools for mid-Cretaceous sections.

Several episodes of accelerated carbon sequestration took place during the Cretaceous as attested by globally distributed OM-rich marine black shales, termed Oceanic Anoxic Events or "OAEs" (Schlanger and Jenkyns, 1976). Six major Cretaceous OAEs have been extensively documented (Fig. 1-2), namely the early Aptian OAE1a, Albian OAE1b, 1c, 1d, Cenomanian – Turonian OAE2, and Santonian OAE3, as well as minor local or regional sub-events which are not as easily detectable in lithologically condensed sections. (Schlanger and Jenkyns, 1976; Arthur et al., 1990; Jenkyns and Wilson, 1999;

Leckie et al., 2002). Previously, these OM-rich sediments had been attributed to the local paleophysiographic arrangement that restricted the inflow of oxygenated water into the respective basin, thus leading to stagnant bottom waters. However, the latter notion does not explain the fact that these OM-rich horizons are found in a great variety of settings, their widespread distribution and their apparent synchronous occurrence (Ryan and Cita, 1977). A comprehensive model that considers several compounding variables provides a better explanation for these quasi-global events: 1) Intense volcanism associated with the rifting of Gondwana and Laurasia coupled with the emplacement of several LIPs led to the effusion of large amounts of CO₂. 2) Strong greenhouse conditions resulted in an ice-free world with reduced oceanic thermal contrasts, limited vertical mixing and a sluggish circulation. 3) Warm SSTs led to out-gassing of dissolved gases, which could have certainly reduced the concentration of dissolved oxygen in the water column. 4) Widespread rifting resulted in a paleogeographic arrangement conducive for the formation of many semi-restricted basins. 5) Intensified global precipitation cycles led to heightened supplies of trace and bio-limiting nutrients (Fe, P) from continental weathering, which could have fueled phytoplankton blooms in marine surface waters. 6) Large fluxes of riverine waters could have led to the development of stratified basins, especially those with already impoverished circulation. 7) Enhanced primary production generated large amounts of OM that remineralized simultaneously with poor mixing of bottom and surface waters, which could have expanded the oxygen minimum zone (OMZ) and thereby resulted in the preservation of extensive OM-rich sedimentary deposits.

1.1 Main Objectives

The Organyà Basin, located in northeastern Spain, developed as a semi-enclosed basin during the early Cretaceous (Fig. 1-3). Previous studies document the onset of the early Aptian OAE1a in medium dark gray (N4) to grayish black (N2) hemipelagic

Figure 1-3 Paleogeographic location of the Organyà Basin during the Aptian. Figure from Sanchez-Hernandez et al. (2014), modified from data by Masse et al. (1993), Mancinelli and Chiocchini (2006) and Godet et al. (2013).

limestones (Fig. 1-4) known as the Cabó Marls (García-Senz, 2002) at the locality of El Pui, near the village of Cabó, in Catalunya, south-central Pyrenees of Spain (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016). Sediments of the Organyà Basin span the entire early Cretaceous (Berriasian to Albian) and the

Figure 1-4 A) Panoramic picture at the locality of El Pui, scale at 2 m. B) Picture of the OM-rich hemipelagic marlstones near the hamlet of El Pujal, scale at 3 m. Notice the parked car on the road adjacent to the easily accessible outcrop.

beginning of the late Cretaceous (Cenomanian/Turonian) (García-Senz, 2002), and consist of over 4,000 m of continuous marine sediments, composed mostly of OM-rich hemipelagic marlstones and shallow-water limestones that accumulated during the evolution of a pull-apart phase of the basin (García-Senz, 2002). Coupled with the excellent exposure (Fig. 1-4A) and ease of accessibility (Fig. 1-4B) to the site, the outcrops in the municipality of Organyà offer the opportunity for detailed, high-resolution studies. The main objectives of this study were:

1) To utilize the expanded and continuous early Aptian deposits outcropping in Organyà, taking advantage of the unique sedimentary conditions that occurred in a marginal setting

of the Basin during this time interval, to understand the lithological and geochemical response to changing paleoenvironmental conditions associated with OAE1a.

- 2) To apply a multi-proxy approach to broaden our understanding of the local factors particular to the Organyà Basin, which maintained continuous deposition of OM-rich sediments in relation to OAE1a, their ties to global forcing factors, and determine the possible causes of negative shifts in the $\delta^{13}\text{C}_{\text{org}}$ chemostratigraphic record of the basin.
- 3) To take the opportunity of the high accumulation rate in the Organyà Basin to achieve the important goal of developing a detailed $\delta^{13}\text{C}_{\text{org}}$ curve, calibrated with index fossils, to serve as a correlation tool without the common problems associated with biostratigraphy.

1.2 Questions and Hypotheses

Questions and hypotheses to be tested include:

- 1) What are the possible causes of negative inflections in the $\delta^{13}\text{C}$ record of Cretaceous sediments of the Organyà Basin? Are they global events or local phenomena?

The presence of coeval negative spikes in widely distributed basins points towards a global causal mechanism. Volcanogenically sourced CO_2 and methane hydrates have highly depleted $\delta^{13}\text{C}$ values, $\sim -8\text{‰}$ and $\sim -60\text{‰}$, respectively. While differential fractionation by local photosynthesizers and diagenesis could be mitigating factors associated with negative carbon isotope values, but considering the relatively large magnitude of the negative excursions, it can be hypothesized that these negative inflections are likely the results of large volcanic eruptions and/or the destabilization and release of methane from continental shelves.

- 2) What is the specific response of the semi-restricted Organyà Basin to perturbations of the global carbon cycle during the denouement stages of the early Aptian OAE1a?

Previous studies at El Pui concluded that the Organyà Basin developed as a semi-restricted water body affected by intensified precipitation cycles associated with variable climatic conditions. Field observations of the El Pui section show tightly imbricated successions of limestones and marlstones, while at the El Pujal section lithology changes to widely spaced, differentially weathered packets of limestones, argillaceous limestones and marls. As a result, it can be hypothesized that paleoenvironmental conditions during the deposition of the El Pujal sequence shifted towards longer intervals of variable wet and dry climatic conditions, thus yielding the alternating lithology in addition to possible higher sediment accumulation rates.

3) What are the local factors that resulted in the accumulation of OM-rich sediments in the Organyà Basin during a period of severe oxygen-deficient conditions in the ocean (OAE1a)? Did these regional factors affect the global $\delta^{13}\text{C}_{\text{org}}$ signature in the Organyà Basin?

Previously, the El Pui section (latest Barremian – early Aptian) revealed that regional conditions led to a series of interacting factors that caused OM-preservation: heightened supplies of bio-limiting nutrients Fe, P from continental weathering, which fueled phytoplankton blooms; large fluxes of riverine waters that induced density stratification within the semi-restricted basin; enhanced primary production generated large amounts of OM that simultaneously with poor mixing could have expanded the OMZ through the water column. Thus, it can be hypothesized that a similar mechanism unique to the Organyà Basin could explain the continuous deposition of OM-rich sediments associated with the El Pujal section.

Considering that intervals of enhanced continental weathering and discharge of riverine waters must have increased the flux of terrestrially derived OM linked with depleted $\delta^{13}\text{C}_{\text{org}}$ values ($\sim -26\text{‰}$ to -28.5‰), it can be hypothesized that these intervals were linked with minor ($\sim < 1\text{‰}$) negative shifts in the $\delta^{13}\text{C}_{\text{org}}$ curve.

4) Are the sedimentary and geochemical signals recorded in the El Pujal section strictly locally unique to the Organyà Basin, or are these signals regionally expressed in neighboring basins?

The Organyà Basin developed because of extensional faulting in relation to the syn-rotational rifting that occurred along the northern portion of the Iberian plate during the early Cretaceous. Extensional faulting created a series of elongated depocenters, including the Basque-Cantabrian Basin, the North Pyrenean Basin and the Central Pyrenean Basin which itself harbors the Organyà Basin. Therefore, it can be hypothesized that regional paleoclimatic, paleoceanographic and, in particular, regional sea level changes, should show parallelisms between these locally unique, but regionally and tectonically connected basins.

1.3 Summary of the Basis for the Proposed Approach

To accomplish the proposed objectives and test my hypotheses the following generalized approach was developed:

- 1)** Extensive fieldwork was undertaken to understand the overall tectonic and structural setting of the area, as well as to identify small and large-scale facies changes, and sedimentary structures that indicate depositional conditions.
- 2)** High-resolution sampling was employed with the intent of characterizing the minor and major temporal perturbations recorded during this interval of the Organyà Basin.

3) Petrographic analysis of thin sections under binocular and scanning electron microscopy (SEM) was used as a complement to field observations, to evaluate mineral content, microfacies changes, and for concentration and identification of microfauna. Smear slides were used to examine the calcareous nannoflora content, fine fraction of the matrix, and for possible index nannoflora taxa identification.

4) Quantification of total inorganic carbon (TIC) was used to assess the contribution of carbonate producers to the rocks.

5) Organic matter preservation in marine sediments is a complex process that depends on a series of mechanisms that are usually not mutually exclusive, including: rate of primary production, source of OM (labile or recalcitrant), sedimentation rate, sediment grain size and oxygen content. Therefore, quantification of the total organic carbon (TOC) provides a general idea of the magnitude of these variables.

6) The application of stable carbon isotope relies on the kinetic fractionation of the two main stable isotopes of carbon, ^{12}C (98.89%) and ^{13}C (1.11%). During photosynthesis, these non-radiogenic isotopes are fractionated in proportions that follow the kinetically favored path where the lighter ^{12}C isotope is preferentially extracted from the system in comparison with ^{13}C . Therefore, organically derived carbon is depleted in ^{13}C relative to the atmospheric $^{13}\text{C}/^{12}\text{C}$ ratio. During periods of enhanced organic matter sequestration, large quantities of OM enriched in ^{12}C are removed from the oceanic reservoir, which becomes enriched in ^{13}C . Hence, autotrophs will then fix carbon with enriched values of ^{13}C , given that the heavier molecule has become more abundant in the reservoir. High-productivity events, which sequester large amounts of OM, such as those related to OAEs, are therefore recorded in the $\delta^{13}\text{C}_{\text{org}}$ chemostratigraphic record as positive

excursions. Furthermore, since these autotrophs uptake CO₂ from the global carbon pool, the curves document shifts that signal overall simultaneous responses of temporal changes in the global carbon reservoir. Consequently, the $\delta^{13}\text{C}_{\text{org}}$ curve is used to identify OAEs, and for correlation of widely distributed sections.

7) Major terrestrially derived elements including aluminum (Al), silicon (Si) and titanium (Ti), termed “lithophiles” (Goldschmidt’s classification) are elements that have strong affinity for oxygen and form compounds that do not sink to the core and are thus enriched in the Earth’s crust. On that basis, their concentrations are used as clues to assess the input of terrigenous fluxes into the basin.

8) Bio-limiting elements including iron (Fe) and phosphorus (P) are essential nutrients used by phytoplankton during photosynthesis and for other biochemical processes.

Surface waters are usually depleted in these elements and thus their availability exerts a control on phytoplankton productivity. The concentration of these elements (Fe, P) helps to estimate the nutrient content in the basin during deposition.

9) Redox-sensitive trace elements (RSTEs) including vanadium (V), nickel (Ni), Cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo) and uranium (U), are elements that under reducing conditions form organometallic complexes, complex with sulfides, or form insoluble hydroxides and thus become enriched in sediments that accumulated under such conditions. The concentrations of RSTEs are used here as a proxy to evaluate the oxygen level in the paleoenvironment, which is one of the most critical variables in the development of OM-rich deposits.

10) Biomarkers are organic molecules preserved in rocks or sediments that retain all, or part, of their parent structure. Biomarkers are used here as proxies to determine the

source of the OM, reconstruct the depositional environment, and determine thermal maturation.

11) Bulk and clay mineral analyses were used to assess the mineralogical composition of the rock matrix, climate, and relative intensity of weathering and runoff from landmasses adjacent to the Organyà Basin.

1.4 Dissertation Structure

The main body of the dissertation covered in Chapters 4 to 7 are organized as chapters representing separate research articles that address the objectives and questions stated above. These chapters are either published, in press, or submitted for publication.

- Chapter 1 – Covers general background information of Cretaceous OAEs, main objectives of the dissertation, questions and hypotheses, summary of the basis for the chosen methodology and the structure of the dissertation.
- Chapter 2 – Explains the tectonic evolution of the Organyà Basin.
- Chapter 3 – Describes in detail the specific materials and methods applied to accomplish the objectives and answer the proposed research questions.
- Chapter 4 – Adds supplementary data in a high-resolution study of the interval that includes the negative intra-C2 CIE in the El Pui section to complement earlier works (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016).

The geochemical characteristics of the *n*-alkanes in the negative shift are analyzed in order to assess whether local biogeochemical factors were involved. In addition, plausible causal factors are proposed.

- Chapter 5 – Investigates the lithological and geochemical response of the Organyà Basin hemipelagic El Pujal section in relation to perturbations of the global carbon

- cycle during segment C5 of OAE1a. Paleoenvironmental and paleoclimatic models are proposed to integrate regional and global forcing factors influencing the continuous accumulation of OM-rich sediments at El Pujal.
- Chapter 6 – Discusses the influence of regional paleoenvironmental conditions on OM sequestration and analyzes how the input of terrestrial vegetation linked with lower values of $\delta^{13}\text{C}_{\text{org}}$ may have altered the global $\delta^{13}\text{C}_{\text{org}}$ archive in the Organyà Basin.
 - Chapter 7 – Investigates the response of the Organyà Basin to changing paleoenvironmental conditions related to the end of carbon isotope segment C5. Documents regional paleoclimatic, paleoceanographic and, in particular, regional sea level changes that may be responsible for synchronous facies variability recorded in the Organyà Basin and at coeval sites in the Basque-Cantabrian Basin. Integrates the sedimentary and geochemical signals recorded at the El Pujal section within a broader spatial frame in order to establish parallels and differences that may help in assessing the regional expression of global perturbations associated with OAE1a.
 - Chapter 8 – Summarizes the general conclusions and importance of this investigation.

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2 GEOLOGIC EVOLUTION OF THE ORGANYÀ BASIN

From the late Jurassic to the early Cretaceous the opening of the North Atlantic Ocean led to the separation of the Iberian Plate from Eurasia and Africa (Fig. 2-1) (Srivastava et al., 1990; Olivet, 1996; Vergés et al., 2002; Sibuet et al., 2004). Concurrent with this rifting phase, the Bay of Biscay opened, leading to the counter-clockwise rotation of Iberia by $\sim 35^\circ$ and a sinistral translation of Iberia relative to Eurasia (Fig. 2-1) (Van der Voo, 1969; Williams, 1975; Montadert et al., 1979; Montigny et al., 1986; Srivastava et al., 1990; Sibuet and Collette., 1991; Choukroune, 1992; Rosenbaum et al., 2002; Sibuet et al., 2004; Gong et al., 2008; Vissers and Meijer., 2012). The syn-rotational rifting along the northern portion of the Iberian plate produced significant

Figure 2-1 Plate kinematic reconstruction of Iberia (IB) relative to Europe (EU) during the Tithonian, Late Aptian and Santonian. The syn-rotational rifting of Iberia relative to Europe produced extensional faulting that generated the Organyà Basin. Figure from Jammes et al. (2009).

extensional faulting which generated a series of elongated depocenters, including the Basque-Cantabrian Basin, the North Pyrenean Basin and the Central Pyrenean Basin (Puigdefàbregas and Souquet, 1986; Berástegui et al., 1990; Vergés and García-Senz., 2001; García-Senz., 2002). From the late Cretaceous onwards, the convergence between Africa, Iberia and Europe brought about the closure and subsequent inversion of these Mesozoic extensional depocenters, which presently lie parallel and on the north and south

Figure 2-2 A) Location map of the Organyà Basin in the Iberian Peninsula. B) Regional geologic map showing the area of interest. A) and B) modified from Dinarès-Turell and García-Senz (2000). C) Detailed geologic map of the studied area showing the location of the El Pui section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) and the El Pujal section. C) Modified from Gong et al. (2009).

Pyrenean zone (Fig. 2-2) (Vergés and Muñoz, 1990; Muñoz, 1992; Vergés and García-Senz., 2001; García-Senz 2002; Golonka, 2004).

The Organyà Basin forms part of the Central Pyrenean Basin and thus represents one of these extensional depocenters (Berástegui et al., 1990; García-Senz, 2002). During the early Cretaceous, the Basin was located on the northern margin of the Ebro block with an estimated area measuring at least 15 km wide and about 70-100 km long along its

Figure 2-3 Generalized stratigraphic column of the Organyà Basin with geomagnetic polarity time scale (GPTS) after Gradstein et al. (2004) and lithostratigraphic units and formation thicknesses after García-Senz (2002). General figure after Gong et al. (2009).

extensional axis (Dinarès-Turell and García-Senz, 2000; Vacherat et al., 2017). While relatively small, it accommodated an impressive 4,000 m sequence consisting of shallow platform carbonates and hemipelagic to pelagic marine sediments (Fig. 2-3) (Berástegui

et al., 1990; García-Senz, 2002). Sedimentary successions are recorded from the upper Tithonian until the lower Turonian (Fig. 2-3), after which the basin fill was inverted and transported southward above a detachment fault in a compressional phase linked with the Pyrenean orogeny (Vergés and García-Senz., 2001; García-Senz, 2002).

In its present position, the Organyà Basin is part of the South Pyrenean Central Unit (SPCU), which itself is comprised of the Bóixols and Montsec thrust sheets, the Cotiella and Pedraforca nappes and the Sierras Marginales thrust sheets (Seguret 1972; Vergés and Muñoz, 1990; Puigdefàbregas et al., 1992; García-Senz, 2002). Remnants of the Basin outcrop in the hanging wall of the Bóixols thrust system, bounded to the north by the Morrerres backthrust (Fig. 2-2C) (García-Senz, 2002; Gong et al., 2009). Along its center, a prominent E-W trending asymmetric syncline (Santa Fé syncline) divides the northern, relatively thick limb from a thinner southern limb (Fig. 2-2C) (Gong et al., 2009).

2.1 Locations and General Descriptions of the Study Sites

The investigated sections include the El Pui and El Pujal sections, both of which are located on the northern limb of the Santa Fé syncline, in the municipality of Organyà (Fig. 2-2C). The El Pui section is located at 42° 14' 36.00"N and 1° 13' 33.67"E on the southern flank of the Sierra de Prada. As described in Sanchez-Hernandez and Maurrasse (2014), erosion by the Cabó River exposes the series of hemipelagic marlstones, organic-rich marls and limestones known as the Cabó Formation (García-Senz, 2002) in dip slope topography. The El Pujal composite section, projected to be sequentially continuous with

Figure 2-4 Satellite and outcrop images of the entire El Pujal section covered in this study. Red rectangles labeled A, B, C and D correspond to the location where the outcrop photographs were taken.

the El Pui section (Fig. 2-2C), is precisely situated at $42^{\circ}13'06.15''\text{N}$ and $1^{\circ}18'55.85''\text{E}$

and consists of the basal 13.77 m-interval (Fig. 2-4), the middle 70.75 m-interval (Fig. 2-4), and the uppermost 85.82 m-interval (Fig. 2-4). Stratigraphically, the El Pujal sequence is placed within the uppermost Cabo marls that extend ~ 950 m within the Aptian (Fig. 2-3) (García-Senz, 2002). In general, the section includes a continuous and expanded sequence of OM-rich hemipelagic sediments exposed as differentially weathered packets in a scarp slope topography with ~ 64° southwest dipping beds that allow exceptionally easy, high-resolution temporal analysis of the succession (Fig. 2-4). The section is well exposed and easily accessible via the Avenida Santa Fé road, which stems from the main town of Organyà.

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3 MATERIALS AND METHODS

3.1 Field Sampling

El Pui section – In 2011, Yosmel Sanchez-Hernandez conducted a field collection of samples analyzed for the El Pui section discussed in Chapter 4 of the dissertation. Sample collection involved systematic bed-by-bed description, including rock colors using the Munsell color system (Goddard et al., 1963), field scale sedimentary and tectonic structures and measurement of bed thickness with a measuring tape (Sanchez-Hernandez, 2014). Samples were taken at least 5 cm deep from the surface and labeled in continuous numeric order with the year of collection as reference (Sanchez-Hernandez, 2014).

El Pujal section – I carried out sample collection for the El Pujal section over a three-year period, 2015, 2016, and 2017. The lowermost 13.77 m-interval (0 m – 13.77 m) sampled in 2015 achieved a total sample collection of 42 hand specimens at an average resolution of one sample every 33 cm. The middle 70.75 m-interval (14.29 m – 85.04 m) sampled in 2016 achieved a total sample collection of 109 hand specimens at an average resolution of one sample every 65 cm. The uppermost 85.82 m-interval (86.07 m – 171.89 m) sampled in 2017 achieved a total sample collection of 106 hand specimens at an average resolution of one sample every 81 cm. Samples were collected by targeting apparent beds and by removal of the top ~ 1 m surface to ensure collection of unweathered rocks. Samples were systematically labeled with the letter C, indicative of the locality (Cabó), followed by the year of collection and ending with the corresponding continuous numeric order. Bed thickness was measured with a measuring tape and sample positions were recorded in individual photographs for accuracy in determining their stratigraphic positions and as a reference during subsequent analyses. Field-scale

descriptions included bed geometry, sedimentary and tectonic structures, lithology, and abundance, type and preservation of macrofossils. Field-scale color description of samples is based on the modified Munsell color system as proposed by Goddard et al. (1963).

3.2 Microscopic Analyses

3.2.1 Thin Sections

At least one thin section per sample was prepared for petrographic analysis. Microscopic analysis of thin sections was conducted using an Olympus BH-2 light transmitting microscope. Selected thin sections were gold (Au) sputter coated using an SPI-MODULE sputter coater and examined using a JEOL JSM 5910LV scanning electron microscope (SEM). Thin section analysis focused on microfacies, mineralogical composition, index fauna identification, bioturbation and presence/absence of benthic fauna and minerals indicative of redox conditions. The micropaleontological analysis for planktonic foraminifera was accomplished primarily using the help of illustrations in the published literature (e.g. Verga and Premoli-Silva, 2002; Heldt et al., 2008; Moullade et al., 2015). Visual estimates of allochems follow Shvetsov's proposed percentage diagrams as summarized by Terry and Chilingarian. (1955). Color description of thin sections used the modified Munsell color system proposed by Goddard et al. (1963). A bioturbation index was assigned to each sample following the proposed scheme in Taylor and Goldring (1993). In addition, the benthic fauna, focusing on benthic foraminifera and echinoid fragments was counted in samples; the total counts were divided by the area of each thin section and are expressed as density (ρ) or number of specimens per cm^2 . In addition, certain samples (refer to Chapter 7) were selected to be counted for the ratio

between planktonic and benthic foraminifera as a tool to estimate paleodepths. The ratio is expressed as the percentage of planktonic foraminifera or %P and depth is calculated using the relationship between bathymetry and %P as proposed by van der Zwaan et al. (1990):

$$\text{Depth (m)} = e^{(3.58718 + (0.03534 * \%P))}$$

The %P is the percentage planktonics in the total foraminiferal association, calculated as $100 * P / (P + B)$, where P is the number of planktonic individuals and B is the number of benthic individuals.

3.2.2 Smear Slides

Smear slides were prepared for various samples to test for the presence of calcareous nannofossils (refer to Chapters 4 and 5). Samples were prepared by placing a drop of deionized water (DI) on a clean glass slide and using a wood toothpick, a small amount of sample material was placed on the drop of water and smeared on the slide. The slide was placed on a hot plate at 70°C until all of the water was evaporated and only a barely visible veneer of sample was left behind. Afterwards, two drops of epoxy were placed on top of the sediment veneer, avoiding contact with the slide to prevent contamination. A cover slip was placed on the slide and then the slide was transferred to cure at 70°C for 30 min. Once completed, smear slides were examined using an Olympus BH-2 light transmitting microscope.

3.2.3 Micropaleontological Work

Small cubes (2.5 cm x 2.5 cm) from selected samples (see Chapter 5) were placed in a 30% solution of acetic acid (CH₃COOH) and left for approximately 24 hrs or until they completely disaggregated. The residue was washed through 150 µm, 63 µm, and 38

µm filters and mounted on slides. Slides with mounted specimens were examined using a Wild Heerbrugg binocular reflective light microscope. Some specimens were picked, Au sputter coated, and examined under the SEM.

3.3 Geochemical Analyses

3.3.1 Sample Powdering Procedure

To prepare the samples for geochemical analyses, they were cut using a wet diamond-cutting saw into 1 cm x 1 cm cubical pieces, making sure to remove any visible surface weathering and then placed in an oven at 60°C to dry overnight (~ 12 hrs) . Following that, samples were ground to a fine powder and placed in sealed glass vials. To prevent cross contamination of samples the mill's chamber was cleaned with DI water, wiped with a Kimwipe and acetone then air-dried using compressed air.

3.3.2 Total Carbon/Carbonate/Organic – TC/TIC/TOC

Samples were analyzed using a LECO CR-412 carbon analyzer following the methodology proposed by Gaona-Narvaez et al. (2013), Sanchez-Hernandez and Maurrasse (2014) and modified as proposed by Socorro and Maurrasse (2019). The LECO CR-412 instrument uses an infrared cell to measure the total CO₂ produced by the combustion at 1450 ±2C° of 0.3000g of a powdered rock sample (Gaona-Narvaez et al., 2013). Calibration of the instrument was performed by producing a 15-point, best-fit calibration curve (0.0500g, 0.0700g, 0.1000g, 0.1200g, 0.1500g, 0.1700g, 0.2000g, 0.2200g, 0.2500g, 0.2700g, 0.3000g, 0.3200g, 0.3500g, 0.3700g, 0.4000g) using pure calcite ≥ 99.0 % (C64-500, Fisher Scientific)(Sanchez-Hernandez and Maurrasse, 2014). Accuracy of the instrument was verified by analyzing reference standard materials (Dolomitic Limestone NIST 88b, Calcite C64-500). To obtain TC measurements,

0.3000g of powdered sample material was weighed out and processed in the carbon analyzer. To obtain TIC measurements, 0.3000g of powdered sample material was weighed out, placed in a furnace at 560°C for 2 hrs to remove the organic portion of the sample, and then processed in the carbon analyzer. The TIC results are expressed as CaCO₃%. TOC is then determined by subtracting (TC-TIC), but since the analyzer reports the results as CaCO₃% the difference is also divided by 8.33, which is the molecular weight of CaCO₃ divided by the molecular weight of carbon (100.086/12.011). Hence, the results for TOC are reported as C wt%.

3.3.3 Stable Carbon Isotopes ($\delta^{13}\text{C}_{\text{org}}$)

Approximately 1g of powdered sample material was placed in a previously cleaned (combusted at 560°C for 2 hrs), 12-dram vial and treated with 10% hydrochloric acid (HCl) to remove the inorganic carbon (CaCO₃). The sample was centrifuged, and the supernatant removed. The process was repeated until no carbonate reaction was visible. Subsequently, the sample was vortexed three to five times with DI water, centrifuged for 5 mins and the supernatant removed. This process was repeated until the supernatant reached a pH of ~ 7. The sample was then put in an oven to dry at 60°C, and then homogenized into a powder using an agate mortar and pestle. The homogenized and dried sample was then placed in a vial, ready for the isotopic analysis. The $\delta^{13}\text{C}_{\text{org}}$ values of the samples were measured using an elemental analyzer isotope ratio mass spectrometer (EA-IRMS). Values are expressed on a per mil (‰) basis relative to the Vienna Pee Dee Belemnite standard (VPDB).

3.3.4 Major and Redox-Sensitive Trace Elements

The preparation and calibration outlined here follows the rapid and sensitive method developed for routine analysis of trace elements on sediments and soils proposed by Arroyo et al. (2009). One gram (1.0000g) of previously powdered sample material was weighed out in a polypropylene snap cap tube and spiked with two standard solutions, 350 μ L [1000 ppm] scandium oxide and 300 μ L [1000 ppm] indium metal. The tubes were vortexed for 1 min and left to dry for 48 hrs at 80°C. Once dried the samples were powdered and homogenized once again using a tungsten ball-mill for 30 min, and pressed into pellets using a hydraulic press. Pellets were analyzed using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the FIU Trace Evidence Analysis Facility (TEAF) using a quadrupole ELAN DRC II (Perkin Elmer LAS) in the standard operation mode. Sample ablation was achieved using a 266nm Nd-YAG laser (LSX 500, CETAC) with a 200 μ m spot size and 10Hz. The same pellet was ablated four times in different locations and the raw data integrated using the Glitter software. Analytical performance of the method was evaluated by running three standard reference materials (NIST2710, PACS-2, NIST2704) at the start, every 10 samples, and at the end of the analysis.

3.3.5 Biomarkers: *n*-Alkanes

Before commencing, all of the lab glassware was washed with tap water and soap, then rinsed three times with DI water and heated in the oven at 560°C for 2 hrs. Five grams (5g) of powdered sample material was weighed out, transferred to a mortar and pestle, and further homogenized. The 5g of homogenized sample was transferred to a 12-dram vial with the addition of a 10 ml mixture of (1:9) methanol

(MeOH)/dichloromethane (DCM). The vial was sonicated for 30 mins and then centrifuged for 10 mins until the supernatant completely separated from the pellet. The supernatant was then transferred to a 4-dram vial and 10 ml of fresh 1:9 MeOH/DCM was again added to the 12-dram vial and the mixture sonicated a second time for 30 mins. The cloudy mixture was centrifuged for 10 mins and the supernatant was pipetted out and combined with the first extract in a 4-dram vial and labeled as total lipid extract (TLE). Activated copper was added to the TLE vial to remove any elemental sulfur. The copper was activated by placing it in 10% HCl until it reached its peculiar bright color and then washed 3 times with DI water and 3 more times with DCM. The copper was left in the TLE until it turned completely black ~ 3-4 hrs and then it was removed. The TLE was concentrated by evaporation until almost dry, and then ~ 12 drops of hexane were added. Following that, a glass pipette was plugged with pre-combusted (560°C for 2 hrs) glass wool, filled with 0.5g of 230-400 mesh silica gel, and conditioned with 6 ml of hexane. The TLE was mounted on the column and eluted with 4 ml of hexane to collect fraction F1 containing the aliphatic components (*n*-alkanes).

The samples were analyzed at the FIU Advanced Mass Spectrometry Facility. Separations were achieved by gas chromatography (GC) (Agilent 6890), using method 1506GEO2. M. A volume of 5 μ L of each sample was injected in split-less mode. Injector temperature was set at 280°C and temperature program was as follows: hold at 65°C for 2 mins, increase to 300°C at a rate of 4°C/min, and hold at 300°C for 8 mins. Detection was performed by a single quadrupole mass spectrometer (MS) (Agilent 5973) operating in positive mode electron impact ionization (EI+). Scan range was from m/z 42 to m/z 500 and a solvent delay time of 4 mins.

3.3.6 Biomarkers: Hopanes and Steranes – GC/MS

Selected samples (refer to Chapter 6) were further purified for the analysis of hopanes and steranes through the removal of *n*-alkanes. The *n*-alkanes were isolated from the branched and cyclic hydrocarbons using urea adduction. For this, an aliquot from the aliphatic fraction (F1) (refer to section 3.3.6 for extraction and separation) was combined in a ratio of 2:1 hexane/acetone (4 ml hexane/2 ml acetone) in a previously cleaned (combusted at 560°C for 2 hrs) 11-dram vial. To this, 2 ml of a urea saturated methanol (MeOH) solution was added drop-wise. The saturated urea MeOH solution was prepared by dissolving 16.6g of urea in 100 ml of MeOH at 60°C. The dropwise addition of the urea saturated MeOH solution resulted in the immediate precipitation of white urea crystals. The mixture was allowed to settle overnight and then centrifuged at 2,000 rpm for 5 min to separate the non-adduct fraction from the urea crystals. The non-adduct fraction was collected and stored in a second 11-dram vial. The dry urea crystals were then washed with 3 ml of a 2:1 hexane/acetone solution and the resulting non-adduct solution was combined with the original non-adduct fraction. The urea adduction procedure was repeated three times on the non-adduct fraction to ensure that all the *n*-alkanes were removed. At the end, the non-adduct fractions containing branched and cyclic hydrocarbons (including hopanes and steranes) were combined and evaporated to ~ 1 ml before GC/MS analysis.

Analysis of the non-adduct fraction focused on hopanes and steranes and was conducted at the FIU Advanced Mass Spectrometry Facility. Separation was performed using an Agilent 6890 GC equipped with an UI HP-5MS UI 30 m, 0.250 mm, 0.25 µm, capillary column. Injections (5 µL) were performed in split-less mode with an injector

temperature of 280°C. The oven temperature program was set to hold at 65°C for 2 min. Then ramped to 300°C at a rate of 4°C/min and hold at 300°C for 8 min. Detection was performed by using a single quadrupole mass spectrometer (Agilent 5973) operating in EI+ mode. The instrument was operated in selective ion monitoring (SIM) with a dwell time of 40 ms and a solvent delay time of 4 min. Identification of analytes was achieved on the basis of comparison of published retention times and mass spectra (Watson et al., 2000; Peters et al., 2005, 2007).

3.3.7 Biomarkers: Hopanes and Steranes – GC-MS/MS

Selected samples (refer to Chapter 7) were analyzed for hopanes and steranes. Extraction and separation followed the methodology outlined in section 3.3.5 “Biomarkers: *n*-alkanes”. The separated aliphatic fraction (F1) was concentrated down to 1 ml and stored at 4°C in amber vials before analysis.

The analysis was conducted at the FIU Advanced Mass Spectrometry Facility using a Bruker EvoQ GC triple quadrupole (TQ) MS in metastable reaction monitoring (MRM) mode (MRM-GC-MS/MS). A 1 μ L volume of each sample was injected in split-less mode through an HP-5MS 60 m, 0.25 mm, 0.25 μ m, capillary column. The injector temperature was set at 260°C and the oven was programmed from 65°C for 2 min, followed by a temperature ramp of 4°C/min up to 310°C and held isothermally for 10 min. Metastable transitions of C₂₇, C₂₈, C₂₉, C₃₀, C₃₁, C₃₂, C₃₃, C₃₄ and C₃₅ hopanes included m/z: 370 $\rightarrow$ 191 (370.40 $\rightarrow$ 191), 384 $\rightarrow$ 191 (384.40 $\rightarrow$ 191), 398 $\rightarrow$ 191 (398.4 $\rightarrow$ 191), 412 $\rightarrow$ 191 (412.40 $\rightarrow$ 191), 426 $\rightarrow$ 191 (426.40 $\rightarrow$ 191), 440 $\rightarrow$ 191 (440.40 $\rightarrow$ 191), 454 $\rightarrow$ 191 (454.50 $\rightarrow$ 191), 468 $\rightarrow$ 191 (468.50 $\rightarrow$ 191), and 482 $\rightarrow$ 191 (482.50 $\rightarrow$ 191), respectively. Metastable transition of C₂₇, C₂₈, C₂₉, C₃₀ steranes included m/z: 372 $\rightarrow$ 217

(372.40→217), 386→217 (386.40→217), 400→217 (400.40→217), and 414→217 (414.40→217), respectively. The compounds were identified by comparing retention times and elution patterns with GC-MS/MS results from literature references (Peters et al., 2005, 2007; Ahmed et al 2013).

3.3.8 Biomarkers: Polycyclic Aromatic Hydrocarbons (PAHs)

Particular samples (refer to Chapter 6) were chosen for quantification of polycyclic aromatic hydrocarbons (PAHs). Certified deuterated surrogate PAH mixture (Z-014J-0.5x), p-Terphenyl-d14 internal standard (M-525-FS-2) and perylene standard solution (H-121S) were purchased from AccuStandard (New Haven, CT, USA). Additional standard mixture EPA 525 PAH Mix A and PAH Mix CRM47543 were purchased from Sigma-Aldrich (St. Louis, Mo, USA). Standard solutions were refrigerated at 4°C until needed.

Exactly 5.0000 g (dry weight) of each powdered sample was weighed and transferred to a cleaned (combusted at 560°C for 2 hrs) 11-dram vial. To validate the extraction method and efficiency, 100 µL of the diluted (1 ng/µL) deuterated surrogate PAH mixture (acenaphthene-d10, chrysene-d12, perylene-d12, phenanthrene-d10) was added to each vial prior to solvent extraction. Then, 10 ml of a 1:9 mixture of MeOH to DCM was added to each vial and sonicated for 30 min. Each sample was then centrifuged at 2,000 rpm for 10 min and the sediment-free supernatant transferred to a 4-dram vial. The latter process was repeated with 10 ml 1:9 MeOH/DCM fresh solvent and the extracts combined in the 4-dram vial. Following the extraction, activated copper was added to each extract until the copper turned a black color (~ 3 - 4 hrs), signifying complete reaction with elemental sulfur after which it was removed. The copper was

activated by placing it in 10% hydrochloric acid (HCl) solution for approximately 5 min and then washed three times with DI water and three more times with DCM. The total extracts were concentrated by evaporation until almost dry and then solvent-exchanged with 1 ml of hexane. Separation of the aliphatic fraction (F1) from the aromatic fraction (F2) was achieved using a silica gel-packed glass pipette, first eluted with 4 ml of hexane to remove the aliphatic components (F1) and subsequently eluted with 4 ml of DCM (F2). The second fraction (F2) containing the targeted PAHs was evaporated until almost dry and re-dissolved in 100 μ L of DCM containing the internal standard, p-Terphenyl-d14 (1 ng/ μ L). In addition, for quality control purposes, 3 additional samples were prepared following the previous procedure: A method blank containing only the deuterated surrogate PAH mixture (1 ng/ μ L), a fortified blank containing the deuterated surrogate PAH mixture (1 ng/ μ L) and the targeted PAH standards (1 ng/ μ L) and a fortified sample containing a powdered sample, the deuterated surrogate PAH mixture (1 ng/ μ L) and the targeted PAH standards (1 ng/ μ L).

The PAH analyses were conducted at the FIU Advanced Mass Spectrometry Facility. Sample injection and GC separation were performed by an Agilent 6890 gas chromatograph equipped with an autosampler and an HP-5MS UI 30 m, 0.250 mm, 0.25 μ m, capillary column using Ultra-pure 6.0 helium as the carrier gas maintained at a constant flow of 1 mL/min. The sample was introduced in splitless mode with a purge time of 1 min. The oven temperature was maintained at 70 °C for 2 min and then programmed to increase to 150 °C at 30°C/min and then to 310 °C at 4 °C/min, where it was held isothermally for 10 min. Detection was performed by a single-quadrupole mass spectrometer (Agilent 5973) using EI+ mode. The mass spectrometer was operated under

selective ion monitoring (SIM) mode with two or three ions per target PAH or deuterated PAH. A calibration curve was prepared by serially diluting the standard solutions to prepare 6 calibration standards of increasing concentrations: 25 µg/L, 50 µg/L, 100 µg/L, 500 µg/L, 1000 µg/L, 3000 µg/L. The internal standard, p-Terphenyl-d14 was introduced by serially diluting the stock solution to yield a concentration of 1000 µg/L. The obtained quadratic calibration equations (all $R^2 > 0.99$) were then used to quantify the unknown samples. Concentrations are reported in nanograms per gram of initial dry weight (5.0000 g) powdered-rock (ng/g dw). The serially diluted EPA 525 PAH Mix A was used as an initial calibration verification standard (ICVS), allowing a percent recovery ranging from 80-120%.

3.3.9 Clay Mineral Analysis (<2 µm Fraction)

Specific samples (refer to Chapters 6 and 7) were selected to be analyzed for their clay mineral components. The X-ray diffraction (XRD) analysis of samples was performed at the Illinois State Geological Survey (ISGS) within the Geochemistry Section, Prairie Research Institute, University of Illinois. Samples were gently ground, sieved and the < 250-µm fraction was collected. Subsequently, 15g of the sample was dispersed in 100 ml DI water for 24 hrs. The next day the sample was transferred to a mixer and mixed for one minute. The suspension was then poured back into the beaker and allowed to settle overnight. The next day, one-third of the clear supernatant was poured off and fresh DI water was added. Two drops of dispersant (sodium hexametaphosphate) were added to the suspension and stirred for one minute. After 15 mins, the suspension was transferred on to a glass slide using an eyedropper and dried overnight. All slides were then saturated using ethylene glycol vapors for 48 hrs. The

oriented and glycolated clay slides were analyzed with a Scintag® XDS2000 diffractometer. Step-scanned data were collected from 2° to 34° 2 θ with a fixed rate of 2° per minute with a step size of 0.05° 2 θ for each sample. All resulting traces were analyzed using the semi-quantitative data reduction software from Materials Data Inc. (MDI) known as Jade+®.

3.3.10 Bulk Mineral Analysis

Samples for bulk mineral analysis (refer to Chapter 7) were prepared and analyzed via X-ray diffraction (XRD) method at the Illinois State Geological Survey in the Prairie Research Institute of the University of Illinois. For the analysis, samples were micronized with DI water for 10 min in a McCrone micronizing mill. To remove the majority of the DI water, the samples were transferred to 50 ml tubes and centrifuged for 20 min at 2000 rpm, after which the clear supernatant was poured off. The remaining sample was dried overnight at 40°C, homogenized with a mortar and pestle and packed into an end-loading sample holder as a random powder bulk-pack. The prepared samples were analyzed on a Scintag XDS2000 diffractometer with data collection set from 2° to 60° 2 θ with a fixed time of 5 seconds per 0.05° 2 θ for each sample. The intensity of the identified mineral phases including quartz, potassium feldspar (K-feldspar), plagioclase feldspar (P-feldspar), calcite, dolomite, siderite, pyrite/marcasite and bulk clay were analyzed using the semi-quantitative data reduction software Jade+ and reported as relative percent.

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4 CHARACTERIZATION OF THE NEGATIVE CARBON ISOTOPE SHIFT IN SEGMENT C2, ITS GLOBAL IMPLICATIONS AS A HARBINGER OF OAE1A

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Abstract

Lower Cretaceous C-isotope records show intermittent negative/positive spikes, and consistent patterns of coeval chemostratigraphic curves thus document shifts that signal simultaneous responses of temporal changes in the global carbon reservoir. The standard pattern registered by the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ in Lower Aptian sediments includes distinct isotope segments C1 to C8 (Menegatti et al., 1998). In the El Pui section, Organyà Basin, Spain, C-isotope segment C2 is the longest interval preceding segments C3 – C6 associated with oceanic anoxic event 1a (OAE1a), and reveals a distinct negative shift of $\sim 1.8\text{‰}$ to $\sim 2.23\text{‰}$ defining the C-isotope pattern within that interval. Total inorganic carbon (TIC), total organic carbon (TOC), $\delta^{13}\text{C}_{\text{org}}$, microfacies, *n*-alkanes show no difference before, during, or after the negative inflection. The biomarkers indicate that organic matter (OM) mainly originates from algal/microbial sources because short-chain length homologues ($\leq n\text{C}_{19}$) dominate. $n\text{C}_{20}$ through $n\text{C}_{25}$ indicate some contribution from aquatic vegetation, but little from higher plants ($>n\text{C}_{25}$), as also suggested by the terrestrial/aquatic ratio of *n*-alkanes or (TAR) = $[(nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})]$ (averages 0.085). We suggest that conjoint pulses of contemporaneous LIPs (Ontong Java) and massive explosive volcanism in northeast Asia, the Songliao Basin (SB-V), best conform to plausible causes of the negative intra-C2 carbon isotopic excursion (CIE)

at that time. Because of its apparent common occurrence, the intra-C2 inflection could be a useful marker harbinger to the more pronounced CIE C3, the hallmark of OAE1a.

4.1 Introduction

Variations in the carbon isotope record of Lower Cretaceous deposits are widely recognized to show intermittent prominent negative and positive shifts. The consistency in the pattern of coeval chemostratigraphic curves thus documents shifts that signal overall simultaneous responses of temporal changes in the ocean carbon reservoir. The original standard pattern registered by the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy in Lower Aptian sediments of the Alpine Tethys was subdivided into distinct isotope segments defined as C1 to C8 by Menegatti et al., (1998), a pattern that has been extensively replicated elsewhere and has been calibrated with dependable microfossils at different Tethyan sections (Menegatti et al., 1998; Moullade et al., 1998; Kuhnt et al., 1998; Erba et al., 1999; de Gea et al., 2003; Erba, 2004; Weissert and Erba, 2004; Godet et al., 2006; Li et al., 2008; Najarro et al., 2010; Stein et al., 2011, 2012; Papp et al., 2013; Erba et al., 2015; Moullade et al., 2015). The El Pui section of the semi-restricted Organyà Basin, south central Pyrenees, shows an exceptional record of the lower Aptian hemipelagic sediments coincident with the interval of time of carbon isotope segments C1 to C6 including more than 240 m of uninterrupted sedimentation (Sanchez-Hernandez and Maurrasse, 2014; 2016). This expanded record reveals the details of temporal variations in the Organyà Basin and the global ocean reservoir prior to, and during the Early Aptian prominent oceanic anoxic event 1a (OAE1a), including the short episode not possible to be observed in condensed sections (e.g. 1 - 5 m in the Italian and Swiss sections, Menegatti et al., 1998). This remarkable expanded succession displays lengthened carbon

isotope segments (Sanchez-Hernandez and Maurrasse, 2014; 2016) commensurate with the conventional initial segments (Menegatti et al., 1998). Segment C2 is particularly well developed in the El Pui section (Fig. 4-1, Fig. 4-2D), as it extends ~147.5 m altogether, between about 15.5 and 163 m (Sanchez-Hernandez and Maurrasse, 2014; 2016). The expanded C2 segment also reveals a distinct carbon isotope negative anomaly of ~ 0.5 to 2.06‰ with the lowest values recorded over an approximate interval of 5.3 m (~73.0 – 78.3 m) (Fig. 4-3). Hence, this carbon isotope excursion heralds the ensuing interval where the lowest values occur that correspond to segment C3 at the onset of oceanic anoxic event 1a (OAE1a) (C3 – C6) (Sanchez-Hernandez and Maurrasse, 2014; 2016). A review of the literature reveals that the negative shift within C2 seems to also occur at widely different sites in the Tethyan domain (e.g. Djebel Serdj, Tunisia, Heldt et al., 2008; the Comanche platform, western Texas, United States, Phelps et al., 2015; Phelps, 2011; the Santa Rosa Canyon, Mexico, Li et al., 2008) (Fig. 4-2A, B, C). Because the negative intra-segment C2 carbon isotopic excursion (CIE) in the Organyà Basin can also be identified in carbon isotope curves elsewhere, we hypothesized that the CIE further concur with previous inference (Sanchez-Hernandez and Maurrasse, 2016) and the anomaly may be related to a global phenomenon.

In such a case, the deviation might represent the record of a weak pulse of geochemical changes in the ocean waters that affected the global carbon reservoir.

Figure 4-1 Panoramic view of El Pui section showing the approximate position of carbon isotope segments C1, C2 and C3 correlative with similar chemostratigraphic segments defined by Menegatti et al. (1998).

However, because of the apparent greater magnitude of the shift recorded in the El Pui section (Fig. 4-2), the question arises as to whether local factors in the Organyà Basin might have affected the negative shift within segment C2, or whether it is a genuine record of a short-lived perturbation in the global ocean reservoir harbinger to OAE1a?

As shown in Table 4-1, here we present additional data in a high-resolution study of the interval that includes the intra-C2 CIE in the El Pui section (Fig. 4-2, Fig. 4-3) in complement to earlier works (Sanchez-Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014). Our main goal is to decipher the geochemical characteristics of *n*-alkanes in the negative shift in order to assess whether or not local biogeochemical factors were involved, and its potential use as a sub-event that may be well defined when sampling spacing permits in non-condensed sections. To address the question we used

Figure 4-2 Carbon isotope curve comparing the intra-segment C2 negative excursion of four different locations. A-Djebel Serdj, Tunisia: Modified from (Heldt et al., 2008). B-Comanche Platform, USA: Modified from Phelps et al. (2015). C-Santa Rosa Canyon, Mexico: Modified from Li et al. (2008). D-El Pui, Spain: Modified from Sanchez-Hernandez and Maurrasse (2016).

intervening samples (Table 4-1) not previously analyzed that provide additional total organic carbon (TOC), total inorganic carbon (TIC), $\delta^{13}\text{C}_{\text{org}}$, *n*-alkanes, microscopic analyses with petrographic microscope and SEM, that increase data resolution within an interval of 61 m (39 to 100 m, Fig. 4-3, Fig. 4-4) in the section in order to better constrain the characteristics prior to, during, and after the negative intra-C2 CIE (Fig. 4-3, Fig. 4-4).

4.2 Geologic Setting

Previous studies of the Organyà Basin in Catalunya, northeastern Spain, concur that it developed as a Lower Cretaceous semi-restricted water body associated with a pull-apart tectonic system that lasted approximately 25 million years until the Late Albian (Bernaus et al., 2003). Overall, climatic conditions were tropical to subtropical at a paleogeographic latitude of approximately 25 to 30° above the Equator (García-Senz, 2002). The Basin accommodated a sedimentary succession that includes over 4,500 m of mostly hemipelagic marls toward the depocenter, and mixed heterozoan/photozoan-dominated skeletal limestones in adjacent carbonate platforms (García-Senz, 2002; Sanchez-Hernandez and Maurrasse, 2016). The unusual thickness of the sequence thus implies that the basin experienced extreme subsidence coupled with rapid sedimentation in a pull-apart setting (Sanchez-Hernandez and Maurrasse; 2014; 2016). The basin fill became inverted in the final tectonic phase of collision between the Iberian plate and Western Europe due to the northward movement of Africa toward the close of the Mesozoic (Seguret, 1972; Peybernès, 1976; Muñoz et al., 1984; Berástegui et al., 1990; García-Senz, 2002; Capote et al., 2002; Golonka, 2004; Gong et al., 2009; Sanchez-

Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014; Quintana et al., 2015).

The sedimentary remnants of the uplifted Organyà basin are now exposed in the uppermost unit known as the Bòixols thrust sheet, a component of a series of thrust sheets that comprise the south-central Pyrenees (García-Senz, 2002). The El Pui sequence (coordinates: 42° 14' 36.00"N, 1° 13' 33.67"E) is part of the asymmetrical Santa Fe syncline (García-Senz, 2002), southern flank of the Sierra de Prada. As described in Sanchez-Hernandez and Maurrasse (2014), erosion by the Cabó River exposes the series of hemipelagic marlstones, organic-rich marls and limestones known as the Cabó Formation (García-Senz, 2002) in dip slope topography that allows exceptionally easy high-resolution temporal study of the succession (Fig. 4-1).

The sedimentary record in the Organyà Basin tells the history of the entire Early Cretaceous, particularly the Aptian that comprises more than 1000 m of continuous sediment accumulation. Sedimentation occurred during extreme greenhouse conditions of the Early Cretaceous when the world experienced reduced latitudinal temperature gradients, coupled with accelerated hydrological cycles and intensified continental weathering and runoff (Haq et al., 1987; Huber et al., 1995; Ando et al., 2008; Duque-Botero and Maurrasse, 2005).

The initial micropaleontological study of the El Pui section revealed only very rare identifiable planktonic foraminifera, mostly *Globigerinelloides blowi* (Sanchez-Hernandez and Maurrasse, 2014), nominate zonal marker of the Early Aptian biozone calibrated with the Early Aptian prior to OAE1a. Further study (Sanchez-Hernandez et al., 2014) that focused on the lower part of the El Pui section indicates that carbon isotope

segment C2 is in calcareous nannofossils Biozone NC 6 (Sanchez-Hernandez et al., 2014), which is also assigned to the Early Aptian (Roth, 1978). The sediment is dominated by *Watznaueria barnesae*, particularly below stratigraphic level 30 m (> 60%), but this taxon decreases above that level to ~ 30% and stays steady through the interval comprising the intra-C2 CIE (Sanchez-Hernandez et al., 2014). These authors also reported several nannoconid taxa as an important component of the carbonate matrix, and the nannoconid group increases concomitantly with the decrease in *W. barnesae* that parallels the interval with marked dominance of the wide-canal nannoconid group over the narrow canal group (Sanchez-Hernandez et al., 2014), therefore the change in taxonomic dominance occurred before the well-known nannoconid crisis associated with levels above segment C2.

The carbon isotopic subdivision registered by the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ curves globally has now become widely accepted as the standard pattern of chronology in the Lower Aptian sediments that have been calibrated with reliable planktonic foraminifera and nannofossils biostratigraphy at other Tethyan sections (Menegatti et al., 1998; Moullade et al., 1998; Kuhnt et al., 1998; Erba et al., 1999; De Gea et al., 2003; Erba, 2004; Weissert and Erba, 2004; Godet et al., 2006; Najarro et al., 2010; Stein et al., 2011, 2012; Papp et al., 2013; Erba et al., 2015). Therefore, the chemostratigraphic curve of the carbon isotope is used here to determine chronologic correlation of the El Pui sequence with sections elsewhere (Fig. 4-2). Compatibility in the chronostratigraphic position of

the carbon isotopic segments thus permits to reduce biochronologic inconsistencies

(Reboulet et al., 2006; Millán et al., 2009; Moreno-Bedmar, 2010; Reboulet et al., 2012).

Table 4-1 TIC, TOC, $\delta^{13}\text{C}_{\text{org}}$, and TAR and Pr/Ph values in the El Pui section. The lowest value of the negative CIE occurs at a height of 77.2 m, corresponding to sample C-11-202. Samples with asterisks belong to values measured by Sanchez-Hernandez and Maurrasse (2014; 2016).

Sample ID	Height (m)	TIC	TOC	$\delta^{13}\text{C}_{\text{org}}$	TAR	Pr/Ph	Sample ID	Height (m)	TIC	TOC	$\delta^{13}\text{C}_{\text{org}}$	TAR	Pr/Ph
C-12-223*	100.2	50.3	1.8	-24.24	—	—	C-11-161*	57.9	65.5	0.8	-24.15	—	—
C-12-222*	99.2	50.8	2.1	-24.04	—	—	C-11-160	57.4	61.2	0.5	-24.27	—	—
C-12-221*	97.4	78.9	1.7	-24.7	—	—	C-11-159*	57	57.9	0.7	-24.55	—	—
C-12-220*	96.1	57.1	2.4	-24.03	—	—	C-11-158	56.7	63.2	0.4	-25.25	—	—
C-12-219*	95.4	47.8	2.1	-24.33	—	—	C-11-157*	56.3	52.6	0.7	-24.27	—	—
C-12-218*	94.2	46.2	2.1	-24.78	—	—	C-11-156	56.1	66.2	0.8	-25.02	—	—
C-12-217*	93.6	52.9	1.4	-24.18	—	—	C-11-155*	55.6	66.4	0.7	-23.82	—	—
C-12-216*	92.5	59.8	1.4	-24.13	—	—	C-11-153*	55.1	63.5	0.8	-23.53	—	—
C-12-215*	90.9	43.2	1.7	-24.44	—	—	C-11-152	54.9	63.0	0.6	—	0.00	1.26
C-12-214*	90.2	42.8	1.8	-24.32	—	—	C-11-151*	54.3	52.9	0.8	-23.98	—	—
C-12-213*	89.5	44.5	2.0	-24.22	—	—	C-11-150	53	63.8	0.5	—	—	—
C-12-212*	88.9	55.6	0.4	-23.95	—	—	C-11-149*	52.6	65.0	0.7	-23.44	—	—
C-12-211*	88	69.0	0.8	-24.48	—	—	C-11-148	52	63.8	0.5	—	—	—
C-12-210	87.3	44.7	1.7	-24.08	—	—	C-11-147*	51.6	77.7	0.5	-23.79	—	—
C-12-209*	86.6	64.3	2.0	-24.73	—	—	C-11-146	51.5	74.2	0.5	—	—	—
C-12-208	86	61.9	1.5	-24.84	—	—	C-11-145*	51.3	67.9	0.4	-24.1	—	—
C-11-207*	84.5	64.9	0.6	-25.33	—	—	C-11-144	51	72.2	0.6	—	—	—
C-11-206	83.1	68.9	0.6	—	0.00	1.22	C-11-143*	50.8	68.5	0.5	-24.2	—	—
C-11-205*	81.1	58.1	0.7	-25.36	—	—	C-11-142	50.6	70.6	0.6	—	—	—
C-11-204	79.6	67.5	0.3	-25.74	0.00	0.71	C-11-141*	50.3	71.0	0.4	-24.19	—	—
C-11-203*	78.3	59.1	0.7	-25.89	—	—	C-11-140	49.9	71.0	0.6	—	—	—
C-11-202	77.2	69.0	0.5	-26.26	0.00	1.02	C-11-139*	49.5	67.6	0.5	-24.18	—	—
C-11-201*	75.7	59.6	0.7	-25.95	—	—	C-11-138	48.9	59.9	0.9	—	—	—
C-11-200	74.1	68.1	0.4	—	0.00	1.40	C-11-137*	48.7	61.5	0.7	-23.9	—	—
C-11-199*	73	77.6	0.6	-25.93	—	—	C-11-136	48.5	68.3	0.7	—	—	—
C-11-198	71.5	70.5	0.4	-25.7	0.00	0.84	C-11-135*	48	75.0	0.6	-24.03	—	—
C-11-197*	70.7	66.9	0.8	-24.45	—	—	C-11-134	47.8	78.8	0.4	—	—	—
C-11-196	70.6	79.4	0.8	—	—	—	C-11-133*	47.3	73.7	0.5	-24.12	—	—
C-11-195*	70.2	80.3	0.4	-25.52	—	—	C-11-132	47.1	76.9	0.6	—	—	—
C-11-194	70	84.3	0.9	—	—	—	C-11-131*	46.9	75.3	0.4	-24.17	—	—
C-11-193*	69.7	84.3	0.3	-24.9	—	—	C-11-130	46.7	70.6	0.6	—	—	—
C-11-192	69.5	77.9	0.7	—	—	—	C-11-129*	46.3	70.0	0.6	-24.13	—	—
C-11-191*	69.3	79.8	0.4	-25.42	—	—	C-11-128	46	71.2	0.6	—	—	—
C-11-190	69	75.7	0.7	—	0.30	1.15	C-11-127*	45.8	72.1	0.5	-23.98	—	—
C-11-189*	68.8	79.4	0.4	-25.47	—	—	C-11-126	45.6	72.7	0.6	—	—	—
C-11-188	68.5	77.4	0.7	—	—	—	C-11-125*	45.5	74.0	0.5	-24.05	—	—
C-11-187*	68.3	82.5	0.4	-24.81	—	—	C-11-124	45.2	81.0	0.5	—	—	—
C-11-186	68	75.2	0.6	—	—	—	C-11-123*	45	75.9	0.6	-24.39	—	—
C-11-185*	67.6	70.4	0.6	-24.6	—	—	C-11-122	44.9	80.0	0.6	—	—	—
C-11-184	67.3	73.0	0.5	—	—	—	C-11-121*	44.4	75.7	0.6	-24.5	—	—
C-11-183*	67	81.5	0.6	-24.55	—	—	C-11-120	44	80.0	0.6	—	—	—
C-11-182	66.5	81.2	0.6	—	0.00	1.11	C-11-119*	43.9	77.3	0.6	-24.5	—	—
C-11-181*	66.3	84.4	0.4	-25.25	—	—	C-11-118	43.7	76.1	0.7	—	—	—
C-11-180	65.8	77.3	0.6	—	—	—	C-11-117*	43.6	80.7	0.5	-24.42	—	—
C-11-179*	65.4	68.5	0.6	-24.32	—	—	C-11-116	43.5	80.3	0.6	—	—	—
C-11-177*	64.7	69.6	0.7	-24.58	—	—	C-11-115*	43.1	81.3	0.5	-24.32	—	—
C-11-176	64.4	66.4	1.2	—	0.00	1.32	C-11-114	42.9	82.4	0.6	—	—	—
C-11-175*	64	69.2	0.8	-24.03	—	—	C-11-113*	42.7	81.7	0.4	-24.33	—	—
C-11-174	63.9	68.9	0.6	—	—	—	C-11-112	42.5	83.6	0.6	—	—	—
C-11-173*	63.6	72.5	0.7	-24.2	—	—	C-11-111*	42.3	80.8	0.5	-24.27	—	—
C-11-172	63.3	76.5	0.5	—	—	—	C-11-110	42	87.7	0.5	—	—	—
C-11-171*	63.1	79.4	0.5	-24.5	—	—	C-11-109*	41.8	80.9	1.0	-24.25	—	—
C-11-170	62.5	73.5	0.9	—	—	—	C-11-108	41.5	88.5	0.5	—	—	—
C-11-169*	62	59.6	0.8	-24.62	—	—	C-11-107*	41.3	85.3	0.4	-24.08	—	—
C-11-167*	60.3	76.5	0.6	-24.43	—	—	C-11-106	40.8	79.4	0.6	—	0.34	0.90
C-11-166	59.5	66.6	0.3	-25.36	0.00	1.30	C-11-105*	40.5	74.1	0.7	-24.2	—	—
C-11-165*	59.1	71.6	0.5	-24.2	—	—	C-11-104	40.1	79.3	0.8	—	0.38	1.00
C-11-164	58.7	60.7	0.7	-25.09	—	—	C-11-103*	39.4	78.1	0.5	-24.27	—	—
C-11-163*	58.3	68.4	0.8	-24.1	—	—	C-11-102	39	75.6	0.7	—	—	—
C-11-162	58.1	69.6	0.4	-24.48	—	—

Figure 4-3 Lithostratigraphy and carbon chemostratigraphy of the El Pui section. A-Simplified chronostratigraphic column. B-Vertical variation in TOC. C-Vertical variation in TIC. D-Vertical variation in $\delta^{13}\text{C}_{\text{org}}$ including the characteristic intra-segment C2 negative excursion denoted with a red arrow.

4.3 Materials and Methods

4.3.1 Microscopy

Additional thin sections in intervening samples (Table 4-1) were made to complement previous materials available for both petrographic and SEM analyses as described in earlier works of the El Pui section (Sanchez-Hernandez and Maurrasse; 2014; 2016; Sanchez et al., 2014).

4.3.2 Total Carbon/Carbonate – TC, TIC, TOC, C-isotope

Total carbon (TC) and total inorganic carbon (TIC) and total organic carbon (TOC) contents for all samples were analyzed at Florida International University using a LECO CR-412 carbon analyzer as described in detail in previous studies (Gaona-Narvaez et al., 2013a; 2013b; Sanchez-Hernandez and Maurrasse, 2014), and TIC/TOC are expressed as CaCO_3 and C-wt% respectively of bulk sediment.

Initial preparation of the samples for carbon isotope was carried at the FIU's sample preparation laboratory, and the isotopic analyses completed at the Stable Isotope Laboratory using a Finnigan Delta C EA-IRMS (with TC/EA). Values are reported according to the standard Vienna Pee Dee Belemnite (VPDB).

In Sanchez-Hernandez and Maurrasse (2014), the TIC, TOC and the $\delta^{13}\text{C}_{\text{org}}$ straddling the negative inflection shown in their Figure 7B, C, D, includes results from thirteen (13) samples covering about 18 m (beginning with C-11-183, at 67 m; C-11-185; C-11-187; C-11-189; C-11-191; C-11-193; C-11-195; C-11- 197; C-11-199; C-11-201; C-11-203; C-11-205; and C-11-207, at 85 m). The pattern of the negative inflection and the recovery was further established with additional data (Sanchez-Hernandez and Maurrasse, 2016, Fig. 3D, 11) with the positive recovery ending at ~ 88.9 m (C12- 212),

thus extending the complete overall inflection event within C2 to 21.9 m. We complemented the dataset with five more intervening carbon isotope analyses (Table 4-1), thereby increasing the accuracy of the pattern of $\delta^{13}\text{C}_{\text{org}}$ variation associated with the intra-C2 negative inflection. Also, our curve greatly increases the chemostratigraphic resolution with 52 additional intervening samples (Table 4-1) analyzed for TC, TIC and TOC, from 39 to 102 m (Fig. 4-3).

4.3.3 Analytical Method for Biomarkers

Soxhlet extraction is the standard method for lipid extraction from solid media. However, this method is very time consuming, requiring 24 hrs per sample just to remove the total lipid extract (TLE) and takes high volumes of solvent, 300 ml or more. A new alternative is the technique of accelerated solvent extraction (ASE). This technique relies on the fact that solvents boil at higher temperatures when they are exposed to higher pressures. As a result, extraction of lipids from a solid media can occur at higher temperatures, leading to better extraction and shortened time (1hr). The only downside to this technique is the high cost of the equipment. As a result, a new extraction method, modified from a method used mainly onboard research drilling vessels, was used in the present study.

4.3.3.1 Lipid Extraction

Before commencing the procedure, all of the lab glassware was washed with tap water and soap, then washed 3 times with deionized water and put in the oven at 560°C for 2 hrs to remove any remaining organic matter. A piece of each hand sample was cut into small cubes, approximately 1 cm by 1 cm and allowed to dry overnight at 50°C in the oven. After drying, the samples were ground to a powder using a Bell-Art micromill

and stored in labeled glass vials. 5 grams of powdered rock were transferred to a mortar and pestle and further homogenized. The 5 grams of homogenized sample was transferred to a 12-dram vial and to that, a 10 ml mixture of (1:9) methanol (MeOH)/dichloromethane (DCM) was also added. The vial was then sonicated for 30 min and then the sediment was allowed to settle. The cloudy supernatant was removed and passed through a glass Pasteur pipette plugged with pre-combusted (560°C) glass wool.

In the following step, 10 ml of fresh 1:9 MeOH/DCM was again added to the 12-dram vial and the mixture was sonicated a second time for 30 min. The cloudy supernatant was removed and filtered as before. Both extracts were combined in a 4-dram vial where activated copper was added to remove any elemental sulfur. The copper was activated when placed in 10% HCl until it reached its peculiar bright color and then washed 3 times with deionized water, and 3 more times with DCM. The copper was left in the TLE until it turned completely black ~ 3-4 hrs and then it was removed. The TLE was then concentrated by evaporation until the total volume reached ~ 1 ml.

4.3.3.2 Separation

To recover the non-saponifiable lipids (neutral lipids) the sample was saponified with 10% methanolic KOH solution (5ml) for 1hr at 60°C. The sample was then transferred to a separatory funnel and extracted 3 times with hexane. The top layer (hexane + neutral lipids) was collected and concentrated to less than 1 ml and stored for further fractionation. In the subsequent step, a glass pipette was plugged with pre-combusted (560°C) glass wool, filled with .5 grams of 230 - 400 mesh silica gel, and conditioned with 6ml of hexane. The neutral lipid extract was loaded onto the column

and eluted with 5ml of hexane. This fraction, F1, containing the hydrocarbons (*n*-alkanes) was stored in a glass vial for GC/MS analysis.

4.3.3.3 GC/MS Parameters

The samples were analyzed by GC (Agilent 6890), using method 1506GEO2.M. A volume of 5 μ L of each sample was injected in splitless mode. Injector temperature was 280°C and temperature program was as follows: hold at 65°C for 2 min, increase to 300°C at a rate of 4°C/min, hold at 300°C for 8 min. Detection was performed by a single-quadrupole mass spectrometer (Agilent 5973) operating in positive mode electron impact ionization (EI⁺). Scan range was from *m/z* 42 to *m/z* 500 and solvent delay time was 4 min.

4.3.3.4 Terrestrial Aquatic Ratio (TAR)

Because land-derived organic matter is less labile, sediments may contain higher proportions of these *n*-alkanes than those from aquatic phototrophs. Previous *n*-alkane $\leq nC_{19}$ are mainly derived from marine planktonic organisms and/or bacterial communities (Forster et al., 2004; Peters et al., 2005) *n*C₂₀ - *n*C₂₅ are mainly derived from aquatic macrophytes both marine and non-marine (Cranwell, 1984) and *>n*C₂₅ are mainly derived from terrestrial plants (Cranwell, 1982). It has also been shown that C₂₇, C₂₉, and C₃₁ *n*-alkanes derived from epicuticular land plant waxes could be an important source of lipids in the sediments (Eglinton and Hamilton 1967; Cranwell 1973; Rieley et al., 1991a; 1991b; Bourbonniere and Meyers, 1996). The presence of C₁₇ *n*-alkanes indicates algal contributions (Blumer et al., 1971; Giger et al., 1980; Cranwell et al., 1987; Bourbonniere and Meyers, 1996). Because land-derived biomarkers can enhance light carbon isotopic values, in order to identify the relative contribution of the two different sources in the

terrigenous-aquatic mixture of hydrocarbons in the intra-C2 negative shift of the El Pui section we used the terrestrial aquatic ratio (TAR) of *n*-alkanes as an indicator index (Bourbonniere and Meyers, 1996; Peters et al., 2005; Holtvoeth et al., 2010).

$$\text{TAR} = \frac{n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31}}{n\text{C}_{15} + n\text{C}_{17} + n\text{C}_{19}}$$

Higher TAR values indicate increased land-derived sources of lipid matter relative to aquatic sources.

4.4 Results

4.4.1 Microscopy

Additional petrographic details of the samples in the interval associated with the intra-C2 negative CIE concur with previous detailed petrographic analyses of the 240 m El Pui section (Sanchez-Hernandez and Maurrasse, 2014; 2016). As shown in Figure 4-4, the sediments show persistent isotropic fabric related to bioturbation, and consist of monotonous sparse fossiliferous biomicrite. The overall allochemical components remain unchanged throughout. Visible microfossils (Fig. 4-5) include mostly benthic foraminifera: trochospiral (~100µm); planispiral evolute infilled with framboidal pyrite (~100µm); uniserial (~100µm); biserial (~200µm), roveacrinid fragments (~200µm), and holothurian ossicles (~100µm). SEM analyses of the matrix also revealed a consistent abundance of coccolithophores, as previously discussed in Sanchez-Hernandez and Maurrasse (2014; 2016); Sanchez-Hernandez et al., 2014).

4.4.2 TC, TIC, TOC

The additional analyses (Table 4-1) carried out to complement the previous study (Sanchez-Hernandez and Maurrasse, 2014; 2016) show a TC content that averages

Figure 4-4 Lithology and microfacies of selected samples prior to the lowest value of the intra-segment C2 negative excursion (blue), at the lowest value (red) and after (green). Refer to the legend for a detailed description of each symbol.

77.78% throughout the 39 - 100.2 m interval. As can be seen in Figure 4-3, the TIC for this 61.2 m interval averages 70.2 wt%. Below the negative inflection and shown in blue, the TIC averages 73.1 wt%. The average TIC value within the interval of the negative inflection is ~ 69 wt%, and subsequently the average decreases to 56.6 wt%. Unlike the TIC, the TOC values do not fluctuate as much and stay relatively stable at an average of 0.7 wt%. The average TOC prior to the negative inflection is 0.6 wt%, while at the interval correlative with the negative inflection it measures ~ 0.5 wt%, but interestingly the average increases to 1.4 wt% afterwards.

4.4.3 Carbon Isotope - $\delta^{13}\text{C}_{\text{org}}$

The high-resolution carbon isotope curve concurrent with TIC and TOC curves shown in Figure 4-3 revealed no correlation in the temporal variations of these three components. The $\delta^{13}\text{C}_{\text{org}}$ record shows that the lower part of segment C2 includes values almost steadily around -24‰, reaching two small positive peaks of -23.44‰ and -23.53‰, at 52.6 m and 55.1 m, respectively. From 55.1 m upward, the $\delta^{13}\text{C}_{\text{org}}$ values fluctuate in a high frequency oscillating pattern toward a negative trend between -23.82‰ (~ 55.6 m) and -25.52‰ (70.2 m) with an average of -24.62‰. An ultimate positive increase to -24.45‰ occurs at 70.7 m, preceding a sharp drop to -25.7‰ at 71.5 m that distinguishes a net negative shift of 1.45‰ preceding a further shift to the lowest value of -26.26‰ at 77.2 m, thus yielding a net negative excursion of 1.81‰. From 77.2 m up section, the isotopic values increase regularly up to a maximum of -23.95‰ at 88.9 m (Table 4-1). Hence, if the overall negative excursion is taken between the two highest values comprising the anomaly or more precisely between 64 m ($\delta^{13}\text{C}_{\text{org}}$ -24.03‰) and ~ 89 m ($\delta^{13}\text{C}_{\text{org}}$ -23.95‰) the net negative excursion characteristic of the intra-C2 anomaly

Figure 4-5A A-Trochospiral benthic foram (scale-100 μ m). B-Planispiral evolute benthic foram infilled with framboidal pyrite (scale-100 μ m). C-Roveacrinid fragments (scale-200 μ m). D-Biserial benthic foram (scale-200 μ m). E-Uniserial benthic foram (scale-100 μ m). F-Holothurian ossicle (scale-100 μ m). Figure 4-5B K/L/M/N-Abundance of calcareous nannoplankton plates and fragments in smear-slide (scale-50 μ m) and in SEM micrograph. A- Rare ammonite (cm scale). G-Echinoid spine (scale-100 μ m) B-Rare gastropod (mm scale). C-Small sized planktonic foram [*G. blowi*] (scale-100 μ m).

can be estimated at 2.23‰ in the lowering phase and $\sim$ 2.31‰ in the recovery phase.

Carbon isotopic values in the remainder younger levels of segment C2 fluctuate around -24‰ with minor cyclical variations, as discussed in Sanchez-Hernandez and Maurrasse (2016). As pointed out by these authors, the detailed $\delta^{13}\text{C}_{\text{org}}$ profile of segment C2 therefore encloses a distinct negative shift between 1.81‰, and 2.23‰ preceding the most prominent negative shift up to $\sim$ 4‰ assigned to carbon isotope segment C3 (Menegatti et al., 1998).

Thus, the high-resolution carbon isotope curve in the expanded El Pui section allows to clearly define the intra-segment C2 CIE that provides a pattern that could be used as a reference harbinger to carbon isotope segment C3. At El Pui C3 yields the lowest value of $\sim$ -28.0‰ which has been the minimum recorded in the entire section (Sanchez-Hernandez and Maurrasse, 2016).

4.4.4 Comparison of the Carbon Isotope Curve at El Pui with Other Locations

A review of the $\delta^{13}\text{C}_{\text{org}}$ curves from three different geographic locations, namely the Djebel Serdj Basin in Tunisia (Heldt et al., 2008), the Comanche Platform in the United States (Phelps et al., 2015; Phelps, 2011), the Santa Rosa Canyon section in Mexico (Li et al., 2008) and the El Pui section in Spain (Sanchez-Hernandez and Maurrasse, 2014; 2016), reveals a noticeable negative inflection during carbon isotope segment C2 at each site (Fig. 4-2). A similar inflection seems to occur in the C2 segment of the Italian Gorgo a Cerbara section (Li et al., 2016) but the low accumulation rate at that location masks the overall expression of the pattern.

In the Djebel Serdj Basin (Fig. 4-2) values of the carbon isotope curve are reported from the carbonate fraction (cf. Fig. 3 in Heldt et al., 2008). Segment C2 is coeval with the Lower Aptian *Globigerinelloides blowi* Zone and yields fluctuating $\delta^{13}\text{C}_{\text{carb}}$ values between $\sim 1.8\text{‰}$ and $\sim 0.5\text{‰}$, starting from about stratigraphic level ~ 16 m up to 35 m (low of 0‰ at 25 m, high of 1.5‰ at 30 m, low of 1‰ at 35 m). The maximum positive value of $\sim 1.8\text{‰}$ is reached at 35 m. This positive value is followed by a sudden negative excursion to $\sim -0.35\text{‰}$ at 40 m, and up again to $\sim 0.95\text{‰}$ around 45 m where the values oscillate between 1 and -0.7‰ with an average $\sim 0.3\text{‰}$ prior to the large negative excursion associated with C3 at ~ 71 m ($\delta^{13}\text{C}_{\text{carb}}$ minimum of -1‰). The range of the anomaly in this section is $\sim 2.35\text{‰}$, a magnitude concurrent with the excursion recorded in the El Pui sediments.

Carbon isotope values for the Comanche Platform are also reported from the carbonate fraction (cf. Figure 11 in Phelps et al., 2015). At that location, the lower part of C2 overlaps the Lower Aptian *G. blowi* and *Leupoldina cabri* Zones. The $\delta^{13}\text{C}_{\text{carb}}$ values

range from $\sim 2.4\text{‰}$ in the lowest level to a maximum positive shift to 3.7‰ . Immediately succeeding this high value a negative shift to $\sim 2.7\text{‰}$ distinguishes the transition from the lower part to the upper part of isotope segment C2. Thus, in sediments of the Comanche platform the range of this intra-C2 negative CIE is $\sim 1\text{‰}$. The remainder of C2 yields fluctuating values between 3‰ and 3.5‰ before dropping to the lowest value of 1‰ associated with segment C3 (Fig. 4-2).

The $\delta^{13}\text{C}$ record of the Santa Rosa Canyon section is reported from the organic carbon fraction (cf. Fig. 4 (B) in Li et al., 2008). At that location carbon isotope segment C2 lays within the Lower Aptian *G. blowi* Zone and nannofossil NC6 Zone (Li et al., 2008). Part of the segment C2 reported starts at the stratigraphic height of 116 m with a value of $\sim -23\text{‰}$, which is followed by a minor negative shift to $\sim -24.3\text{‰}$ at ~ 117 m (Fig. 4-2). This negative shift is succeeded by a positive value to $\sim -23.7\text{‰}$ at ~ 118 m. The $\delta^{13}\text{C}_{\text{org}}$ remains relatively stable around -24‰ up to the approximate height of 121 m where the values decrease remarkably to the minimum of $\sim -26.2\text{‰}$ at 124 m. A positive recovery takes place immediately thereafter to the maximum of $\sim -25\text{‰}$ at ~ 125 m, hence forming the characteristic modulation of intra-segment C2 negative shift with an anomaly of $\sim 2.2\text{‰}$ preceding the more negative excursion characteristic of segment C3. The CIE at the Santa Rosa Canyon further concurs with the amplitude of variation recorded at the sites previously discussed and supports the similarity with the Organyà Basin site at El Pui.

While there is an overall similar pattern in all of the sections discussed, it is evident that differences in amplitude could be attributed to local forcing factors such as source of OM, maturation etc. However, to postulate a causal factor with any certitude to explain

the differences in amplitude would require a more detailed geochemical characterization of each of the locations. While this intra-segment C2 CIE may not be very distinct in a number of Lower Aptian sections in the published literature, clearly, factors such as sampling resolution, reduced thickness of section or even hiatuses in sediments during that time interval will affect the occurrence or absence of the inflection.

4.4.5 Lipid Biomarkers

The biomarker results rely on accepted *n*-alkane values attributed to certain biota as follows:

* $\leq nC_{19}$ are mainly derived from marine planktonic organisms and /or bacterial communities (Forster et al., 2004; Peters et al., 2005)

* $nC_{20} - nC_{25}$ are mainly derived from aquatic macrophytes both marine and non-marine (Cranwell, 1984; Ficken et al., 2000; Mead et al., 2005)

* $>nC_{25}$ are mainly derived from terrestrial plants (Cranwell, 1982)

Since the OM shows low maturity (Sanchez-Hernandez and Maurrasse, 2016) we can postulate that the carbon isotopic values $\delta^{13}C_{org}$ are primary with little diagenetic overprinting.

In the interval studied the *n*-alkanes (Fig. 4-6) represent the most abundant fraction of the total extractable lipids from all the samples. In general, the aliphatic fraction is dominated by short chain homologues $\leq nC_{19}$ with a range of $nC_{10} - nC_{30}$ and no apparent odd or even preference. Since the OM shows low maturity (Sanchez-Hernandez and Maurrasse, 2016) and very labile short chain $\leq nC_{13}$ alkanes are present, the results suggest that there has been little to no diagenetic alteration of the *n*-alkanes distribution. Since short chain *n*-alkanes indicate an algal or microbial source, while longer chain

Figure 4-6 Summary of organic geochemistry results and their respective stratigraphic locations along the $\delta^{13}\text{C}_{\text{org}}$ curve. A-Stratigraphic Height vs TAR. B-N-alkane results for selected samples. C-Stratigraphic Height vs Pr/Ph. Colors (blue, red, green) refers to the duration before, during and after the lowest value reached within the intra-segment C2 negative excursion respectively.

$>nC_{25}$ indicates terrestrial plant matter, (Bourbonniere and Meyers, 1996), in the El Pui section the TAR $[(nC_{27}+nC_{29}+nC_{31})/nC_{15}+nC_{17}+nC_{19}]$ values shown in Figure 4-6A (blue color) imply some contribution of terrestrially derived OM at stratigraphic levels 40.1 m (sample C-11-104, TAR = 0.38); 40.8 m (sample C-11-106, TAR = 0.34) and 69 m (sample C-11-190, TAR = 0.3), respectively. At the lowest levels, the *n*-alkanes distribution is slightly bimodal, but sample C-11-190 at 69 m shows a stronger allochthonous input as attested by the abundance of the longer chain *n*-alkanes (Fig. 4-6B). The TAR average for the interval (39 m – 75.7 m), corresponding to the time before the negative inflection is 0.112, whereas at the negative inflection (Fig. 4-6A, B in red), there is a more normal distribution with a range of $nC_{14} - nC_{23}$ and the highest abundance being attributed to nC_{16} . The TAR value at the lowest point (77.2 m) of the negative inflection is zero. Following the negative inflection (Fig. 4-6A, B in green), the *n*-alkanes distribution is dominated by short chain $\leq nC_{19}$ homologues with some minor contribution from aquatic macrophytes, $nC_{20}-nC_{25}$ (bimodal distribution shown in graph C-11-204 (Fig. 4-6A). The *n*-alkanes as well as the TAR of zero corroborate the lack of contribution from terrestrial vegetation. As previously stated, the occurrence of *n*-alkanes ranging from values between nC_{23} to nC_{25} has been shown by several authors to belong to submerged aquatic vegetation, from both marine and non-marine environments. Namely, Ficken et al. (2000) where they looked at lipid extracts from submerged and emergent aquatic plants in freshwater lakes on Mt. Kenya and more recently by Mead et al. (2005) where the authors looked at lipid extracts from submerged and emergent marine/estuarine vegetation in the coastal Everglades region of South Florida. These authors also demonstrated that emergent aquatic vegetation such as mangroves have very similar *n*-

alkanes distribution to terrestrial vegetation, with chain lengths ranging from nC_{26} - nC_{29} .

It is worth noting the unusual abundance of these n -alkanes in two periods constituting to sample C-11-190 (69 m) and C-11-204 (79.6 m). Hence, we conclude that during these two intervals the basin was getting significant input of organic matter from estuarine and or wetlands sources.

The second most abundant molecules present in the aliphatic fraction are pristane (Pr) and phytane (Ph). These acyclic isoprenoids are derived from the phytol side chain of chlorophyll and their concentrations are dependent on the oxygen content, or lack thereof in the water column during deposition. Under reducing conditions, the reaction favors the formation of phytane while under oxidizing conditions pristane is produced (Brooks et al., 1969; Didyk et al., 1978). Ratios of Pr/Ph higher than 1 signify deposition under oxidizing conditions while values lower than 1 indicate dysoxic to anoxic conditions. The Pr/Ph values in the lower portion (Fig. 4-6C) corresponding to the time before the negative inflection indicate that deposition occurred under relatively oxygenated conditions, except for sample C-11-106 and C-11-198, which show slightly dysoxic conditions. During the negative inflection, the Pr/Ph ratio stays slightly above unity, while after the negative inflection a lowest value of 0.71 is observed and then returns to oxygenated conditions with a value of 1.2.

4.5 Discussion

4.5.1 Significance of the n -alkane Distribution in the Intra-Segment C2 Negative Carbon Isotope Inflection

It is well established that elemental carbon includes two non-radiogenic isotopes, ^{12}C (98.89%) and ^{13}C (1.11%), which are fractionated during photosynthesis in

proportions that depend on the method of carbon fixation followed by the organism. Thus, most terrestrial plants undergo C3 photosynthesis, which fixes more light carbon atoms thereby leading to negative $\delta^{13}\text{C}$ values ranging from -24 to -34‰. In phytoplankton and photosynthetic bacteria kinetic fractionation (Guy et al., 1993) is less pronounced thus $\delta^{13}\text{C}$ values are far more positive, ranging from -12 to -23‰. These accepted ranges of carbon isotope values coupled with *n*-alkanes will allow us to find whether there is absence of terrestrial plant influences during the interval of carbon isotope negative shift, or whether the amplitude observed is being “artificially” inflated by allochthonous, terrestrially derived OM.

As previously discussed, when assessing the biological sources of organic matter the basic principle employed relies on the presence of lipid biomarkers that are specific to their origin (Brocks et al., 2005). One such general source indicator is the presence of short versus long chain *n*-alkanes originating from phytoplankton/microbial and terrestrial vegetation, respectively. As can be seen in Figure 4-6B most samples show an *n*-alkane distribution dominated by shorter chain ($n\text{C}_{10}$ - $n\text{C}_{19}$), suggesting that the source of the OM is mostly autochthonous. However, the ratio of allochthonous OM to autochthonous OM shows some temporal changes that include terrestrially derived *n*-alkanes at levels 40.1 m and 40.8 m, respectively (C-11-104, C-11-106), far below the onset of the negative carbon isotope shift (Fig. 4-6B). Similar terrestrial OM recurs at 69 m (C-11-190), shortly prior to, but not coincident with the most negative values characteristic of the intra-C2 CIE. The shorter chain homologues *n*-alkanes derived from phytoplankton/microbial sources that dominate during the negative inflection suggest that the $\delta^{13}\text{C}_{\text{org}}$ curve is not being altered by the input of very light $\delta^{13}\text{C}$ OM derived from

terrestrial plant. These values thus imply that the negative shift can be related to a global perturbation in the carbon reservoir.

In addition to OM source identification, *n*-alkane distribution is also a good index for the relative maturation/degradation state of the OM. Maturation and microbial degradation of OM can alter the *n*-alkane distribution through the selective removal of the more labile, shorter chain *n*-alkanes and thus cause an enrichment in the more recalcitrant, terrestrial plant derived portion. In effect, the predominant phytoplankton/microbial signature ($\leq nC_{19}$) in the *n*-alkane distributions of most of the samples indicates good preservation conditions, therefore lending support that the OM in the basin was most likely preserved with *n*-alkanes that characterize the original composition.

4.5.2 Possible Modulating Factors in the Intra-Segment C2 Negative Excursion

Given the regional and global geologic settings of the Early Aptian, several plausible interactive factors could have been involved in causing the intra-segment C2 negative inflection as follows:

1. - Based on the tectonic history of the area, and given that hydrothermal processes are associated with pull-apart basins (Rubin, 1997; Bjørlykke, 2010) it is plausible that magmatic degassing could have introduced large concentrations of light carbon in the Organyà Basin, thereby affecting the overall carbon isotopic intake in the semi-restricted basin. However, extensive studies of the area do not report evidence of igneous processes (Peybernès and Souquet, 1973; Peybernès, 1976; Martínez, 1982; Muñoz et al., 1984; Caus et al., 1990; Berástegui et al., 1990; Dinarès-Turell and García-Senz, 2000; García-Senz, 2002; Bernaus et al., 2002, 2003; Capote et al., 2002; Gong et al., 2009; Sanchez-

Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014). Furthermore, trace element analyses point rather to terrigenous fluxes in the basin in compatibility with the paleophysiography and climatic conditions at that time (García-Senz, 2002; Sanchez-Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014). Hence, the possibility of local magmatic influence can be ruled out.

2. - Given the semi-restricted setting of the Organyà Basin and extensive terrigenous fluxes associated with conditions at that time (Dinarès-Turell and García-Senz, 2000; García-Senz, 2002; Bernaus et al., 2002, 2003; Sanchez-Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014) such fluxes could account for significant organic molecule input of terrestrial origin. Since dissolved organic matter (DOC) entering the surface waters exhibit tendency to concentrate at interfaces, therefore this DOC could be rapidly adsorbed in contact with particles suspended in sea water and particulate organic matter (POM), thereby being transformed into aggregates and zooplankton feces and settled rapidly (Asper, et al., 1992). This organic matter would therefore be sequestered and the terrestrial origin preserved in the sediments, thus possibly contributing to a light carbon isotopic signature in the record. Also, terrestrial DOC that were rapidly mixed into the upper ocean (Williams and Druffel, 1987; Bauer et al., 1992) and not remineralized (Bauer et al., 1992) could maintain a significant steady input of isotopically light carbon to be fixed by *in situ* primary producers in the euphotic zone. By this process, fixed carbon by photosynthesizers would reflect the effects of terrestrially derived organic matter. Trace elements results indicate oxygen-deficient conditions likely associated with water column stratification (Sanchez-Hernandez and Maurrasse, 2014); therefore, recirculation must have been limited in the

basin. Furthermore, the *n*-alkane results from the interval that includes the intra-segment C2 CIE do not support a land-derived influence in the organic matter supplied into the basin at that time. Thus, this second possibility can be safely excluded as well.

3.- Another possible scenario may invoke external influences affecting the global ocean carbon reservoir, albeit local mitigating factors (accumulation rate, tectonism, strong ecosystem variability) that could overprint *in situ* isotopic ratios not significantly affected by direct input from terrigenous OM. In the latter case, the isotopic signature would be worldwide and the record would mirror the extant isotopic ratio of the global carbon reservoir. Since methane derived carbon is ~12 times lighter (Méhay et al., 2009), Jahren and Ahrens (1998) suggested that gas hydrate dissociation might have caused rapid rate of $\delta^{13}\text{C}$ changes during the negative carbon isotope shifts in Lower Aptian sediments. This possibility remains conjectural because of the long duration of these negative anomalies. On the other hand, recent studies of Lower Cretaceous explosive volcanism in Asia (Songliao Basin or northeast Asia SB-V volcanism; Wang et al., 2002; 2016) appear to be coeval with effusion of the large igneous provinces (Larson, 1991). Thus, the coupled effects of massive LIPs and land volcanism suggest that volcanic CO_2 release in pulses of different magnitudes and duration could have been the driving mechanisms for the worldwide occurrences of negative carbon isotope shifts. Indeed, the signals are also recorded in lacustrine deposits (Zhang et al., 2016), which substantiates the non-strictly marine causal origin for the forcing mechanism of light carbon input into the global carbon reservoir systems. The widespread occurrence of the negative intra-segment C2 CIE at different sites supports the possible combined effects of intermittent pulses of contemporaneous Ontong Java Plateau (OJP) flood basalt and widespread

massive continental volcanism in Asia (Wang et al., 2002; 2016). The results suggest that long lasting global volcanism appears to be the most plausible driving factors that led to the variations observed in the Lower Aptian deposits, including the negative isotope shift in C2.

4.6 Conclusions

Carbon isotope segment C2 in the expanded El Pui section of the Organyà Basin, south central Pyrenees sections of the Tethyan realm includes a marked negative inflection of $\sim 1.81\text{‰}$ to 2.23‰ . Carbon isotope segment C2 is the longest interval preceding the segments assigned to anoxic event 1a (OAE1a) (C3 – C6). TIC, TOC, $\delta^{13}\text{C}_{\text{org}}$, microfacies, paleontological and biomarker (*n*-alkanes) reveal no difference in biota between the time before, during or after the negative inflection. During the negative shift, the *n*-alkanes are predominantly short-chain length homologues with very little to no contribution from shallow marine ($n\text{C}_{20}\text{--}n\text{C}_{25}$), land-derived aquatic vegetation, and absolutely none from higher plants ($>n\text{C}_{25}$). The terrestrial/aquatic ratios TARs $(nC_{27}+nC_{29}+nC_{31})/(nC_{15}+nC_{17}+nC_{19})$ averaging 0.112 before and 0 during the negative inflection indicate that local factors did not enhance the $\delta^{13}\text{C}_{\text{org}}$ negative inflection during C2. Thus, the negative inflection in C2 reflects a true change within the ocean carbon isotopic reservoir independent from local sea level fluctuations at that time. Variations in magnitude and duration of Lower Cretaceous massive explosive volcanism in Asia and northeast Asia SB-V (Songliao Basin) coupled with contemporaneous LIPs offer a plausible explanation for the negative carbon isotopic excursions recorded at El Pui and elsewhere. The intra-segment C2 negative excursion indicating a change in the global ocean reservoir can be a useful chemostratigraphic marker harbinger to OAE1a.

Additional high-resolution studies are required in non-condensed sections to resolve if smaller-scale regional differences in $\delta^{13}\text{C}$ are observed specific to these areas. The results further highlight the value of chemostratigraphy in correlation, and the apparent common occurrence of the intra-C2 inflection implies that it may be a useful anticipatory marker to the more pronounced CIE C3 associated with the onset of OAE1a.

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5 CONTINUOUS ACCUMULATION OF ORGANIC MATTER-RICH SEDIMENTS ASSOCIATED WITH OCEANIC ANOXIC EVENT 1A IN THE EL PUJAL SECTION, ORGANYÀ BASIN, CATALUNYÀ SPAIN AND ITS RELATION TO EPISODIC DYSOXIA

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Abstract

A detailed lithostratigraphic and geochemical analysis was performed on a 13.77 m sequence consisting of a succession of limestones, argillaceous limestones and marlstones at the El Pujal section in the Organyà Basin of the south-central Spanish Pyrenees. Biostratigraphic analysis reveals the presence of the foraminifer *Leupoldina cabri* positioning the sequence within OAE1a. Corroborating evidence from stable carbon isotope data permits the correlation of the El Pujal section with other Tethyan sections, namely Roter Sattel (Switzerland), Cismon (Italy) and El Pui (Spain) to within carbon isotope segment C5. Geochemical results reveal periodic increase of redox sensitive trace elements (RSTEs: V, Ni, Co, Cr, Cu, Mo), biolimiting (P, Fe) and terrestrially derived elements (Al, Si, Ti) at argillaceous limestone and marlstone intervals, concurrent with episodes of enhanced organic matter preservation (TOC >1.18%). Further evidence from microfacies characterized by higher pyrite concentration, impoverished benthic fauna and lower degree of bioturbation are in accord with geochemical proxies. Biomarker data shows *n*-alkanes distributions ranging from *n*C₁₀ to *n*C₃₁, suggesting that the organic matter (OM) is a mixture of *in-situ* produced and terrestrially derived. Calculated average chain length (ACL_{*n*C₂₅-*n*C₃₃}) shows lower values

in intervals associated with argillaceous limestones and marlstones, suggesting wetter climate during these periods. The results imply that fluvial influences controlled by regional hydrologic variability related to climatic fluctuations probably exacerbated the already sluggish basinal conditions through the development of density stratification in the water column. Integration of the data from the El Pujal section shows that changes in paleoproductivity, terrigenous input, and redox conditions characterize the deposition of OAE1a in the Organyà Basin without the hallmark of an anoxic phase. Conditions remained similar to those recorded in the preceding sequence at El Pui, thus revealing continuous deposition of OM under impoverished oxygen conditions, punctuated by episodes of dysoxia.

5.1 Introduction

During the mid-Cretaceous the Earth experienced profound oceanographic and climatic changes (Leckie et al., 2002) attributed to the concurrent paleogeographic reconfiguration associated with continuing rifting of Gondwana and Laurasia which led to the rearrangement of oceanic and atmospheric circulation patterns together with the formation of numerous restricted to semi-restricted basins in the Tethyan realm (e.g. Barron, 1987; Koutsoukos et al., 1991a; Hay, 1995; Poulsen et al., 1999, 2001, 2003). The intense tectonic activity and emplacement of several large igneous provinces (LIPs), such as the Ontong Java Plateau, Kerguelen Plateau and Caribbean Plateau resulted in a marked increase in volcanic outgassing of CO₂ (Arthur et al., 1985; Barron and Washington, 1985; Caldeira and Rampino 1991; Sinton and Duncan, 1997; Leckie et al., 2002; Neal et al., 2008; Tejada et al., 2009) which may also have been determining factors in these changes. Furthermore, the prevailing warm global equable climate led to

reduced oceanic thermal contrasts disrupting vertical mixing while accelerating hydrological cycles, intensifying weathering and runoff. These conditions induced eutrophication of shallow and deep-water environments concurrently with eustatic sea level rise (Barron et al., 1989; 1995; Koutsoukos et al., 1991b; Frakes et al., 1992; Huber et al., 1995; Tarduno et al., 1998; Weissert et al., 1998; Haq et al., 1987). Hence, these factors compounded by a paleogeography particular to many semi-restricted basins led to widespread burial of organic matter (OM) in sediments deposited under dysoxic to anoxic conditions. These relatively brief periods lasting ~1 Myr (Li et al., 2008) of enhanced OM sequestration termed as Oceanic Anoxic Events (OAEs) (Schlanger and Jenkyns, 1976; Jenkyns, 1980) are thus the geologic expression of extreme perturbations in the global carbon cycle. Most importantly, OAEs can also be identified by their distinct global stable carbon isotope signature identifiable in carbonates ($\delta^{13}\text{C}_{\text{carb}}$) and both marine and non-marine organic matter ($\delta^{13}\text{C}_{\text{org}}$) (Erbacher et al., 1996; Hasegawa, 1997; Menegatti et al., 1998; Bralower et al., 1999). Their global isotopic signature thus permits inter-basinal correlation via vertical carbon isotope profiles further constrained through the use of biostratigraphic markers (Wendler, 2013).

As demonstrated in the Organyà Basin of the south-central Pyrenees of Spain, (Fig. 5-1) (Sanchez-Hernandez and Maurrasse, 2014; 2016) the onset of one such event (OAE1a) is recorded in the lower Aptian hemipelagic limestones that outcrop at the locality of El Pui (Fig. 5-1) in the Cabó Formation (García-Senz, 2002). Marine sediments that comprise more than 4,000 m of continuous accumulation filled the Organyà Basin during the entire Early Cretaceous (Berriasian to Albian) through the beginning of the Late Cretaceous (Cenomanian/Turonian) (García-Senz, 2002). The succession consists mostly

of OM-rich hemipelagic marlstones and shallow-water limestones that accumulated during the evolution of a pull-apart phase of the basin (García-Senz, 2002; Sanchez-Hernandez and Maurrasse, 2016). While the extensive published literature indicates that the record of OAE1a shows wide spatial variation, in most locations where the event is recorded its hallmark is a distinct interval of higher OM, laminated sediments, redox sensitive trace elements (RSTE's) peaks, and perturbation or complete absence of benthic life, all indicative features of oxygen-deprived conditions. Furthermore, the onset includes a constant pronounced negative carbon isotopic excursion (0.5-3‰), followed by a positive excursion (>1.5-5‰) believed to be related to primary production and intensified OM burial (Menegatti et al., 1998). Thus, characteristically the event interval is lithologically distinct from interrelated and adjacent sediments, as in most pelagic and hemipelagic settings OAE1a usually documents oxygen-deficient conditions with shales, marls and or bituminous limestones enriched in OM. By contrast, adjacent intercalated limestones are low in OM, and accumulated under fully oxic conditions (Menegatti et al., 1998; Bellanca et al., 2002; Yilmaz et al., 2004; Dumitrescu and Brassell, 2005, 2006; Luciani et al., 2006; Rückheim et al., 2006; Ando et al., 2008; Heldt et al., 2008; Li et al., 2008, and others herein). Other shallow-water carbonate systems experienced severe disruption and drowning (Burla et al., 2008; Heldt et al., 2008), especially in areas of the northern Tethyan region (Funk et al., 1993), in France (Hunt and Tucker, 1993; Masse, 1993), Italy (Bosellini et al., 1999; Graziano, 1999), Spain (Ruiz-Ortiz and Castro, 1998; Gaona-Narvaez et al., 2013), the northeastern North American margin (Jansa, 1993), and in the Texas and Mexican region (Scott, 1993; Lehman et al., 1998). However, in certain areas of shallow-water environments along the southern and central Tethyan realm the

event may not include a distinct lithologic interval as the facies is uninterrupted, showing continuously full oxic conditions (e.g. Grötsch et al., 1998; Chaabani and Razgallah, 2006; Heldt et al., 2010; Huck et al., 2010).

The semi-restricted Organyà Basin also shows no distinct lithologic response to the overall forcing factors generally associated with OAE1a, since the sediments have relatively high total organic carbon (TOC) of up to 1.7% and high total inorganic carbon (TIC) (average 70%) prior and during the event (Sanchez-Hernandez and Maurrasse, 2014; 2016). In the present work, we studied the El Pujal section, which is sequentially continuous with the neighboring El Pui section (Sanchez-Hernandez and Maurrasse, 2014; 2016). The study is a multiproxy analysis where we (1) present new geochemical data for samples associated with the denouement stages of OAE1a, (2) investigate the uninterrupted response of a semi-restricted basin in a hemipelagic setting to perturbations of the carbon cycle during the Aptian and (3) propose environmental and climatic models that integrate regional and global forcing factors influencing the continuous accumulation of OM-rich sediments of the Organyà Basin. The results will provide further understanding on the controlling environmental mechanisms that led to continuous accumulation of OM-rich sediments.

5.2 Geologic Setting

Remnants of the Organyà Basin deposits are presently exposed as part of the uppermost unit of the series of Bòixols thrust sheets that comprise the south-central Pyrenees (García-Senz, 2002). The sequence from the Sierra de Prada that continues in the Santa Fè syncline (Fig. 5-1) includes a complete succession up to the Cenomanian/Turonian (Bernaus et al., 2003). Sediments in the Organyà Basin

Figure 5-1 Detailed geologic map of the study area modified after Gong et al. (2009). Red hexagons show the relative location of the El Pui Section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014; 2016) and the El Pujal Section (this study).

accumulated from the latest Jurassic to the Late Cretaceous (Fig. 5-2) concurrent with the breakup of the supercontinent Pangaea into Laurasia and Gondwana, and the complex tectonic evolution of the Iberian plate (Berástegui et al., 1990; Salas and Casas, 1993; Dañobeitia et al., 1990; Salas et al., 2001; Torsvik et al., 2008). Laurasia included mostly the Iberian plate, North America and Eurasia, while Gondwana comprised South America, Africa, Australia and Antarctica. Rifting continued during the Cretaceous, leading to the opening of the North Atlantic Ocean and the separation of the Iberian plate from Eurasia and Africa (Olivet, 1996, Vergés et al., 2002). During the Early Cretaceous the ~ 30 to 35° counter clockwise rotation of Iberia led to the opening of the Bay of Biscay (e.g., Van der Voo, 1969; Williams, 1975) and the development of several pull-

Figure 5-2 Stratigraphic column of the Organyà Basin showing the span of the El Pui Section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014; 2016) and the El Pujal Section (this study) with geomagnetic polarity time scale (GPTS) after Gradstein et al. (2004) and lithostratigraphic units and formation thicknesses after García-Senz (2002). General figure after Gong et al. (2009).

apart basins, including the Basque Cantabrian Basin, and the Central Pyrenean Basin

together with the Organyà Basin (García-Senz, 2002). Previous studies report that the

Figure 5-3 Paleogeographic map of the early Aptian with the location of the Organyà Basin marked with a red star. Figure modified after Masse et al. (2000).

area was located under a wet tropical to subtropical paleogeographic latitude of approximately 25° to 30° north of the Equator (Fig. 5-3) (Masse et al., 2000). As shown in Figure 5-3, paleogeographic reconstructions indicate that the basin was somewhat restricted by several land masses which provided ample terrigenous influx while experiencing extreme subsidence that allowed for the accommodation of over 4000 m (Fig. 5-2) of mostly hemipelagic marls and platform limestones (Beràstegui et al., 1990; García-Senz, 2002). Near the end of the Mesozoic the northward movement of Africa eventually led to the collision of Iberia with Eurasia, and closure of these Pyrenean basins concomitant with the Alpine orogeny during the Cenozoic (Golonka, 2004). The present work investigates a 13.77 m section starting at the base of outcrops near the hamlet of El Pujal (42°13'06.15"N, 1°18'55.85"E) situated on the southern flank of the Cabó river

valley. The outcrops show a succession projected to be sequentially continuous with the El Pui section, based on three-dimensional views on Google maps. Their position implies that stratigraphically, the succession may be placed within the upper portion of the Cabó marls, approximately correlative with carbon isotope C5 (Sanchez-Hernandez and Maurrasse, 2014; 2016), further extending into the lower portion of the Senyús marls (Fig. 5-2) (García-Senz, 2002).

5.3 Methods

5.3.1 Microscopy

Thin sections ($n = 42$) and smear slides ($n = 11$) were examined using an Olympus BH-2 light transmitting microscope. Selected thin sections were gold (Au) sputter coated using an SPI-MODULE sputter coater and examined using a JEOL JSM 5910LV scanning electron microscope (SEM). Small cubes (2.5×2.5 cm) from selected samples were placed in a 30% solution of acetic acid (CH_3COOH) and left for approximately 24 hrs or until they completely disaggregated. The residue was washed through $150 \mu\text{m}$, $63 \mu\text{m}$, and $38 \mu\text{m}$ filters and mounted on slides. Slides with mounted specimens were examined using a Wild Heerbrugg binocular reflective light microscope. Some specimens were picked, Au sputter coated, and examined under the SEM. Color description of samples was based on the modified Munsell color system (Goddard et al., 1963). Visual percentage estimates are after Terry and Chilingar (1955). Bioturbation index (BI) follows the proposed scheme in Taylor and Goldring (1993). Benthic foraminifera were counted with the intent of assessing the oxygenic conditions at the very bottom of the water column. Their total counts are divided by the area of each thin section and are expressed as benthic foraminifera density (ρ) or number of specimens per cm^2 .

5.3.2 Total Carbon (TC), Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC)

Total carbon (TC) and total inorganic carbon (TIC) were carried out on 42 samples analyzed at Florida International University using a LECO CR-412 carbon analyzer following the procedure detailed in Sanchez-Hernandez and Maurrasse (2014). The method was modified with an additional cleaning procedure for previously used combustion boats to ensure complete removal of residual inorganic portion (CaCO_3). Briefly, used combustion boats were brushed under running water, then placed in a 10% hydrochloric acid (HCl) solution for 3 hrs or until bubbling stopped. The boats were then washed 3 times with deionized water and placed in a furnace at 560°C for 2 hrs to remove any remaining organic matter. The results for TC and TIC are expressed as CaCO_3 wt %.

5.3.3 Lithologic Nomenclature

TIC values were used to assign a general lithologic classification modified from Sanchez-Hernandez and Maurrasse (2014). To allow for a greater range of lithologic units based on field observation of the El Pujal section, here we use TIC values $>73\%$ = limestone; $65-73\%$ = argillaceous limestone; $35-65\%$ = marlstone; $10-35\%$ = calcareous shale; and $0-10\%$ = mudrock/shale. Total organic carbon (TOC) is determined by subtracting (TC-TIC), but since the analyzer gives the results expressed as $\text{CaCO}_3\%$ the difference is also divided by 8.33, which is the molecular mass of CaCO_3 divided by the mass of carbon ($100.086 \text{ g}/12.011 \text{ g}$). Hence, the results for TOC are expressed as C wt%.

5.3.4 Stable Carbon Isotope ($\delta^{13}\text{C}_{\text{org}}$)

Samples ($n = 42$) were cut using a wet diamond saw into 1 x 1 cm cubical pieces making sure to remove any signs of surface weathering, and then placed in an oven at 60°C to dry overnight. Each dried sample was ground for 3 mins in a Bell-Art micro-mill and placed in a sealed glass vial. After each use, to prevent cross contamination of samples the micromill's chamber was cleaned with deionized water, wiped with a Kimwipes tissue paper and acetone then air-dried using compressed air. Approximately 1 g of each sample was placed in a previously cleaned (combusted at 560°C for 2 hrs) 12-dram vial and treated with 10% HCl to remove the inorganic carbon (CaCO_3). The sample was centrifuged, and the supernatant removed. This process was repeated until no carbonate reaction was visible. Subsequently, the sample was vortexed 3 to 5 times with deionized (DI) water, centrifuged for 5 mins and the supernatant removed. This process was repeated until the supernatant reached a pH of ~ 7 . The sample was then put in an oven to dry at 60°C, and then homogenized into a powder using an agate mortar and pestle. The powdered dried sample was then placed in a vial, ready for the isotopic analysis. The $\delta^{13}\text{C}_{\text{org}}$ values of the 42 samples were measured at the Rosenstiel School of Marine and Atmospheric Science (RSMAS) stable isotope laboratory (SIL) using a Costech elemental combustion system interfaced with a Thermo Scientific Delta V Advantage continuous flow isotope ratio mass spectrometer. Values are expressed on a per mil (‰) basis relative to the Vienna Pee Dee Belemnite standard (VPDB).

5.3.5 Major, Biolimiting and Redox Sensitive Trace Elements (RSTEs)

The preparation and calibration applied here followed the rapid and sensitive method developed for routine analysis of trace elements on sediments and soils proposed

by Arroyo et al., (2009). As outlined in Sanchez-Hernandez and Maurrasse (2014), all samples (42) were powdered in the same way as those used for carbon analysis previously described. One gram (1.0000 g) of powder was weighed out in a polypropylene snap cap tube and spiked with two standard solutions, 350 μ l [1000 ppm] scandium oxide and 300 μ l [1000 ppm] indium metal. The tubes were vortexed for 1 min and left to dry for 48 hrs at 80°C. Once dried the samples were powdered once again and homogenized using a tungsten ball-mill for 30 mins and pressed into pellets using a hydraulic press. Pellets were analyzed for concentrations of major elements (Al, Si, Ti), biolimiting elements (Fe, P), RSTEs (V, Ni, Co, Cr, Cu, Mo) and potential redox index elements (Th, U) using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the FIU Trace Evidence Analysis Facility (TEAF) using a quadrupole ELAN DRC II (Perkin Elmer LAS) in the standard operation mode. Sample ablation was achieved using a 266 nm Nd-YAG laser (LSX 500, CETAC) with a 200 μ m spot size and 10 Hz. The same pellet was ablated 4 times in different locations and the raw data integrated using the Glitter software. Analytical performance of the method was evaluated by running 3 standard reference materials (NIST2710, PACS-2, NIST2704) at the start, every 10 samples, and at the end of the analysis. Data for elemental concentration is expressed as absolute concentrations as parts per thousand (ppt) for major terrestrially derived elements and biolimiting elements, and as parts per million (ppm) for RSTEs. Elemental concentrations are not normalized to aluminum in this study because the values obtained can lead to “spurious” correlations between uncorrelated elements, and correlation coefficients can increase or decrease with some cases where they even change signs (Van der Weijden, 2002). It has been recognized in the statistical

analysis of biological samples (Pearson, 1896) that when two ratio variables have the same common divisor (Al in this case) and a correlation coefficient is determined for the two ratio variables, false correlations are produced not because of natural relationships between the two variables, but for arithmetic reasons. For a detailed explanation and case studies on this subject, refer to Van der Weijden (2002).

5.3.5.1 Enrichment of Redox Sensitive Trace Elements (EIs)

As compared to their relative crustal abundances, certain elements consistently show higher concentrations in sediments rich in OM which are widely recognized to be characteristic of reducing environments. The enrichment factor has been used in previous studies (e.g. Turekian and Wedepohl, 1961; Wignall and Myers, 1988; Calvert and Pedersen, 1993; Rimmer, 2004; Brumsack, 2006; Sanchez-Hernandez and Maurrasse, 2014; 2016 and others), to assess the changes relative to the average shale as a proxy for crustal abundance (Turekian and Wedepohl, 1961; Wedepohl, 1971). To ascertain the redox attributes of sediments in the El Pujal section here we use the average value of the background level (Bodin et al., 2007) to estimate the relative enrichment for each RSTE (V, Ni, Co, Cr, Cu, and Mo) based on the following equation:

$$EIs = \frac{[RSTEs]}{[RSTEs]_{background}}$$

where [RSTEs] represents the concentration of each sample in ppm and [RSTEs]_{background} is the average value in ppm of the corresponding RSTE in the entire section. To make comparison between RSTEs as a whole and other proxies, enrichment indexes ($\sum EIs$) were calculated by adding all the EIs of each element at each sample point.

5.3.6 Biomarkers

The procedures followed a modified methodology from Socorro et al., (2017). Before commencing the procedure all the lab glassware was washed with tap water and soap, then washed 3 times with deionized water and put in the oven at 560°C for 2 hrs to remove any remaining organic matter. Samples (n = 42) were powdered in the same way as those used for carbon analysis. Five grams (5 g) of powder was weighed out, transferred to a mortar and pestle, and further homogenized. The 5 g of homogenized sample was then transferred to a 12-dram vial with the addition of a 10 ml mixture of (1:9) methanol (MeOH)/dichloromethane (DCM). The vial was then sonicated for 30 mins and then centrifuged for 10 mins until the supernatant completely separated from the pellet. The supernatant was then transferred to a 4-dram vial and 10 ml of fresh 1:9 MeOH/DCM was again added to the 12-dram vial and the mixture sonicated a second time for 30 mins. The cloudy mixture was again centrifuged for 10 mins and the supernatant was pipetted out and combined with the first extract in a 4-dram vial and labeled as total lipid extract (TLE). Activated copper was added to the TLE vial to remove any elemental sulfur. The copper was activated by placing it in 10% HCl until it reached its peculiar bright color and then washed 3 times with deionized water and 3 more times with DCM. The copper was left in the TLE until it turned completely black ~ 3-4 hrs and then it was removed. The TLE was then concentrated by evaporation until almost dry and then ~ 12 drops of hexane were added. Following that, a glass pipette was plugged with pre-combusted (560°C for 2 hrs) glass wool and filled with 0.5 g of 230-400 mesh silica gel and conditioned with 6 ml of hexane. The TLE was mounted on the

column and eluted with 4 ml of hexane to collect fraction F1 containing the aliphatic components (*n*-alkanes).

The samples were analyzed at the FIU Advanced Mass Spectrometry Facility. Separations were achieved by gas chromatography (GC) (Agilent 6890), using method 1506GEO2. M. A volume of 5 µl of each sample is injected in split-less mode. Injector temperature was set at 280°C and temperature program was as follows: hold at 65°C for 2 mins, increase to 300°C at a rate of 4°C/minute, and hold at 300°C for 8 mins. Detection was performed by a single quadrupole mass spectrometer (MS) (Agilent 5973) operating in positive mode electron impact ionization (EI⁺). Scan range was from *m/z* 42 to *m/z* 500 and a solvent delay time of 4 mins.

5.3.6.1 Terrestrial Aquatic Ratio (TAR)

The terrestrial aquatic ratio (TAR) as originally proposed by Bourbonniere and Meyers (1996) provides clues as to the relative influence of terrestrially derived versus autochthonously produced organic matter and is calculated here by dividing the sum of the longer odd-numbered *n*-alkanes by the sum of the shorter chain odd-numbered *n*-alkanes.

$$\text{TAR} = \frac{n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31}}{n\text{C}_{15} + n\text{C}_{17} + n\text{C}_{19}}$$

Based on this equation higher values > 1 indicate predominance of land-derived OM sources.

5.3.6.2 Carbon Preference Index (CPI)

In ancient sediments the carbon preference index (CPI) is a proxy used mainly to determine the degree of thermal maturation (Bray and Evans, 1961). CPI was calculated as follows:

$$\text{CPI} = \frac{1}{2} \left[\frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{24} + n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32}} + \frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32} + n\text{C}_{34}} \right]$$

5.3.6.3 Average Chain Length of Longer *n*-alkanes (ACL)

Average chain length (ACL) of higher plant's *n*-alkanes (*n*C₂₅-*n*C₃₃) (Poynter and Eglinton, 1990) is a parameter that describes the average number of carbon atoms based on the abundance of the odd numbered carbon chain. Here it is calculated as follows:

$$\text{ACL} = \frac{25 * n\text{C}_{25} + 27 * n\text{C}_{27} + 29 * n\text{C}_{29} + 31 * n\text{C}_{31} + 33 * n\text{C}_{33}}{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}$$

The main source of these longer chain *n*-alkanes are leaf waxes (Riederer and Markstädter, 1996; Koch et al., 2009), and their molecular weight may vary depending on different photosynthetic pathways (C₃ or C₄), type of vegetation and climatic conditions (e.g. Krull et al., 2006; Diefendorf et al., 2017). It has been documented that lipid extracts derived from grasslands tend to be enriched in longer chain *n*-alkanes than those from forest vegetation (Schwark et al., 2002; Zech 2006; Zhang et al., 2006). Furthermore, because the main function of these molecules is to prevent the plant from adverse uncontrolled water loss, *n*-alkanes chain length distribution is also a response to temperature and humidity (Sachse et al., 2006; Hoffmann et al., 2013). Accordingly, higher molecular weight *n*-alkanes are more common in response to warmer climates (Bush and McInerney, 2015), and studies of eastern broadleaf forest trees, *Acacia* and

Eucalyptus, showed that higher temperatures along with aridity are both strong controls on the production of longer-chain-enriched leaf wax (Tippie and Pagani, 2013; Hoffmann et al., 2013). In this study, we use ACL variability as a proxy for the broad identification of terrestrial vegetation as well as for deducing climatic conditions on land.

5.3.7 Correlation Analysis

Correlation coefficients were determined for various proxies using Microsoft Office Excel 2013. The correlation coefficient is based on the Pearson's r equation (1896) expressed as:

$$\text{Correl (X, Y)} = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

where $\bar{x}$ and $\bar{y}$ are the corresponding sample's average. The results of this equation go from a perfect negative correlation (-1), no correlation (0) to a perfect positive correlation (1). Values in between will be labeled as: 0.1-0.3 = weak, 0.4-0.6 = moderate, 0.7-0.9 = strong.

5.3.8 Principal Component Analysis (PCA)

PCA was run on the data to exemplify the major variables controlling prevailing paleoenvironmental and paleoclimatological conditions during the studied time interval. PCA on the integrated proxy dataset was analyzed using the statistical software Past3 (<https://folk.uio.no/ohammer/past/>). Since the variables included in the analysis have different units of measure, and because PCA will emphasize variables with highest variances in component one and two, all variables were standardized. This was achieved by subtracting the average of the variable from the actual value and dividing everything by its standard deviation:

$$Z_i = \frac{X_i - \bar{X}_i}{STDEV_i}$$

where Z_i is the standardized variable value, X_i is the variable's value, $\bar{X}_i$ is the variable's average, and $STDEV_i$ is the variable's standard deviation.

5.4 Results

5.4.1 Field-Scale Lithology

Figure 5-4 Photograph of the top part of the 13.77 m outcrop showing the differentially weathered beds correlated with the simplified lithostratigraphic column.

In outcrop, the section is homogeneously dark gray in color (N6) with no apparent change in color and shows repeated differentially weathered packets composed of more indurated beds followed by softer beds that are apparently argillaceous or marly (Fig. 5-4). On the surface, they display a gray coloration (N6) with streaks of iron oxide, while on a freshly cut face they are medium dark gray (N4) when dry and grayish black (N2) when wet. The soft, flaky appearance only occurs at the surface because it dissipates with

depth as the material becomes more indurated. This cyclical pattern of hard/soft beds continues throughout the section. At the field scale, no macrofossils are visible except for sparsely distributed pyritized burrows and unidentifiable ferruginous bioclasts. In hand samples, the rocks can be described as fine grained, biocalcilites, or carbonaceous limestones. Neither samples show appreciable difference between those taken from the previously discussed indurated and softer beds. The samples show very few visible allochems, mainly ferruginous and pyritized fossils and sparse iron oxide nodules, apparently associated with burrow fillings.

5.4.2 Petrographic Analysis

In thin section, the samples are mainly composed of a fine-grained (micritic) matrix, rich in kerogen, organic matter (OM), pyrite and iron oxide. While the fine-grained nature of the matrix stays unvarying throughout, allochems vary, but are mainly composed of small sized planktonic foraminifera <50 µm, roveacrinid fragments, ostracods, echinoid fragments, microscopic gastropods and bivalves (<100 µm), calcispheres, and benthic foraminifera dominated by a few morphotypes: mainly trochospiral, milioline, biserial and uniserial (Fig. 5-5C). In addition, the first occurrence of the index planktonic foraminifera *Globigerinelloides aptiensis* is recorded at 5.52 m, while *Leupoldina cabri* occurs at 13.77 m (Fig. 5-5A) along with several other morphotypes assigned to the Aptian (Longoria, 1974; Sigal, 1952; Verga and Premoli Silva, 2002; www.mikrotax.org). In smear slide and SEM, calcareous nannoplankton plates and fragments are dominant (Fig. 5-5C24, C25), with additional bioclasts of previously discussed taxa (Fig. 5-5A, C). Although in hand sample the softer layers display no apparent lithological difference with the more indurated layers, upon closer

inspection of the thin section, variations become evident. The softer, easily weathered beds layers (TIC <72.26%, TOC >1.18%) may show a bioturbation index (BI) of 3, fewer bioclasts overall (<10%) associated with a fabric that is slightly anisotropic. They also contain higher proportion of pyrite and pyritized bioclasts (~ 60%), pyritized microscopic gastropods and bivalves (Fig. 5-5C), and higher abundance of calcispheres. However, benthic foraminifera and echinoid fragments become rare with <2 specimens per slide in some cases. The time series count of benthic foraminifera shown in Figure 5-5B illustrate these variations which reveal at least 6 detectable declines in benthic foraminifera p occurring at stratigraphic heights of ~ 1.47 m, 3.68 m, 5.82 m, 7.67 m, 9.78 m, and 12.2 m, respectively. The more indurated, less marly samples (TIC >72.26%, TOC <1.18%) show a BI of 4, almost isotropic allochem distribution, and lower concentration of pyrite (Fig. 5-5). Bioclasts are also more abundant in these samples >20% with less pyritized specimens ~ 40%. In contrast to the softer layers, these samples lack microscopic gastropods or bivalves, contain very few calcispheres, but yield the highest benthic foraminifera p and echinoid fragments.

Figure 5-5 (A) Simplified lithostratigraphic column showing the position of various index planktonic foraminifera, *Leupoldina cabri* - 50µm, *Globigerinelloides aptiensis* - 50µm. (B) Time series count of benthic foraminifera. Notice the lower benthic foraminifera ρ during argillaceous limestone and marlstone intervals. (C) Microscopic images of various microfossils and of the rock matrix. (C.1-100µm, 2-50µm, 3-100µm) Various echinoid fragments in a micritic matrix. (C.4-100µm, 19-200µm, 20-100µm) Petrographic and SEM images of various small-sized gastropods. (C.5-50µm, 6-50µm, 7-50µm, 17-50µm, 18-50µm) Images of different pyritized planktonic foraminifera (undetermined species). (C.8-50µm) Image of a well preserved calcisphere in a micritic matrix. (C.9-50µm, 13-200µm) Pyritized example of small-sized bivalve specimens found along the argillaceous limestone and marlstone intervals. (C.10-50µm, 11-50µm, 12-50µm, 14-50µm, 15-100µm, 16-100µm) Images of benthic foraminifera displaying various morphologies. (C.21-200µm, 22-200µm, 23-200µm) Back scattered electron (BSE) images of the matrix from a representative limestone (21), argillaceous limestone (22) and marlstone (23) sample. Notice the increase in pyrite concentration (lighter colored objects) from the limestone sample to the marlstone. (C.24-10µm, 25-5µm) Secondary SEM images of the matrix at different magnifications. Notice the abundance of coccolith plates and fragments throughout.

5.4.3 Carbon Geochemistry (TC, TIC, TOC, $\delta^{13}\text{C}_{\text{org}}$)

TC values fluctuate between 74.51% and 88.56% throughout the studied section, with all measured values rising above 70%. As shown in Figure 5-6B, TIC stays relatively high, above 60% throughout, averaging 72.26%, (22 samples below the average; 20 above). Here the average is taken as the TIC background value of the section. Thus, based on these values three recurrent lithologies are represented: limestones, argillaceous limestones and marlstones. The harder beds always coincide with those labeled as limestone, and the softer beds concurring with argillaceous limestone and marlstone. TIC has a strong correlation ($r = 0.75$) with benthic foraminiferal ρ , and

Figure 5-6 Stratigraphic correlation of carbon geochemistry data ($\delta^{13}\text{C}_{\text{org}}$, TIC, TOC), major terrestrially derived elements (Si, Al, Ti) and biolimiting elements (Fe, P) with lithology. Red dashed line corresponds to the average value of the individual variable. Gray bars correspond to areas depleted in TIC and enriched in TOC, Si, Al, Ti, Fe and P. Elemental concentrations are reported as absolute values in parts per thousand (ppt).

concurrently shows 6 perceivable fluctuations with values below the background at the respective heights of 1.47 m (72.15%), 3.68 m (72.12%), 5.82 m (62.03%), 7.67 m (67.13%), 9.78 m (67.38%), and 12.2 m (65.33%).

The TOC values vary from a low of 0.80% to a high of 1.73% with an average of 1.18%, which is taken as the background value for this studied section (Fig. 5-6C). TOC shows an inverse correlation with benthic foraminifera ρ ($r = -0.41$) and TIC ($r = -0.65$). Hence, the curve for TOC also shows 6 distinct peaks above the background average (1.18%) with values of 1.42%, 1.48%, 1.68%, 1.26%, 1.28%, and 1.34% respectively correlative with the previously defined 6 intervals.

As shown in Appendix 5A and Figure 5-6A carbon isotopes values show a general negative trend upward in the studied section. The measured $\delta^{13}\text{C}_{\text{org}}$ values fluctuate from a high of -22.55‰ at 0.55 m to a low of -24.23‰ at 13.77 m (Fig. 5-6A), with an overall negative shift of 1.68‰, and an average of -23.61‰ taken as the background value for the studied section. The negative trend is saw-toothed with a slope of -7.36, including minor variations characterized in the following detail (Fig. 5-6A). Carbon isotope values in the lowermost 0.82 m are relatively unvarying with an average of -22.59‰, succeeded by a slight negative shift to -23.20‰ at 1.12 m, and then a return to a positive of -22.84‰ at 1.84 m. The negative trend continues with a shift to -23.34‰ at 2.2 m followed by a rise to -23.05‰ at 2.52 m. Subsequently, the curve fluctuates slightly trending down reaching a low of -24.18‰ at 5.52 m, below the average value, and characterizing a net negative shift of ~ -1.59 ‰. A slight positive change of -23.75‰ recurs at 5.82 m followed by a series of low amplitude positive and negative oscillations down to -24.03‰ at 7.40 m. The interval from 7.67 m to 9.10 m shows a trend of comparatively constant

values with an average of -23.76‰. The curve is punctuated by a minor negative spike (-23.97‰) at 9.48 m continued by a rebound to an average of -23.88‰ between 9.78 m to 11.30 m. Thereafter, another more distinct negative shift reaches -24.20‰ at 11.95 m continued by a discrete positive shift of -24.09‰ and decreasing steadily to the lowest value of -24.23‰ at 13.77 m (Fig. 5-6A; Appendix 5A).

5.4.4 Major Terrestrially Derived Elements, Biolimiting Elements, and RSTEs

Terrestrially derived elemental concentrations in rocks of the El Pujal section show at least 6 episodes of enrichment positively correlated with TOC (Fig. 5-6C, D, E, F; Appendix 5B), but inversely correlated with TIC (Fig. 5-6B, D, E, F) and benthic foraminifera ρ (Fig. 5-5B). Al concentrations vary from a low of 14.63 ppt to a high of 40.50 ppt at 2.52 m and 5.82 m, respectively, with an average value of 22.64 ppt. Si concentrations fluctuate from 40.88 ppt to 106.87 ppt with an average of 62.18 ppt and shows an almost perfect correlation with Al ($r = 0.98$). Ti follows the same pattern as Al ($r = 0.98$) and Si ($r = 0.99$) with a minimum of 0.55 ppt at 2.52 m and a maximum of 1.39 ppt at 5.82 m and a mean of 0.82 ppt, concurrent with the biolimiting elements (Fe, P) shown in Figure 5-6G-H. Fe values average 10.24 ppt and show similar correlation with Al ($r = 0.94$), Si ($r = 0.94$) and Ti ($r = 0.88$) with 6 coincident peaks of enrichment 11.08 ppt, 11.77 ppt, 15.92 ppt, 10.46 ppt, 11.33 ppt and 11.57 ppt (Appendix 5B). Temporal variations in the values of P display a similar pattern but with only 5 correlative heights of enrichment (Fig. 5-6H), which coincide with all the previously defined levels except at 1.47 m where P (0.20 ppt) is slightly below the average value (0.23 ppt). The other 5 stratigraphic heights show peaks above the average with values of 0.28 ppt, 0.40 ppt, 0.25 ppt, 0.26 ppt, and 0.23 ppt, respectively (Appendix 5B).

Figure 5-7 Stratigraphic variation in RSTEs, RSTEs EI, Σ RSTEs EI and Th/U correlated with lithology. Red dashed line corresponds to the average value of the individual variable. Gray bars indicate areas enriched in RSTEs. Elemental concentrations are reported as absolute values in parts per million (ppm).

RSTEs reveal a very similar trend with 6 peaks of enrichment and a positive correlation with terrestrially- derived elements, biolimiting elements and TOC (V, $r = 0.69$; Ni, $r = 0.70$; Co, $r = 0.44$; Cr, $r = 0.44$; Cu, $r = 0.71$; Mo, $r = 0.69$), but an inverse trend to TIC and benthic foraminifera ρ (Fig. 5-5B; Fig. 5-6B, C, D, E, F; Fig.5-7A, B, C, D, E, F). Moreover, relative elemental enrichments were calculated for each RSTE in order to quantify their variations with regards to the background level or average in the section. All RSTEs show increases coeval with the 6 previously discussed levels (Fig. 5-7G; Appendix 5B). For instance, compared to the background average, V shows an enrichment of 1.16, 1.21, 1.74, 1.14, 1.01, at 1.18 m, 1.47 m, 3.68 m, 5.82 m 7.67 m, 9.78 m and 12.2 m, respectively. The calculated enrichment index for RSTEs (ΣEIs) (Fig. 5-7H), yields a positive correlation with TOC ($r = 0.71$), major terrestrially derived elements (Al $r = 0.81$), and biolimiting elements (P $r = 0.80$), but it shows a negative correlation with benthic foraminifera ρ ($r = -0.42$), and TIC ($r = -0.43$). Th/U ratios vary from a low of 1.6 to a maximum value of 3.6 at 5.82 m, with an average of 2.5 (Fig. 5-7I; Appendix 5B). The overall Th/U trend covaries with lithology where highest values appear in marly and argillaceous layers, as shown in the following correlations; TOC ($r = 0.30$), major terrestrially derived elements Al ($r = 0.61$), biolimiting elements P ($r = 0.44$), and RSTEs V ($r = 0.54$); however, it shows a negative correlation with benthic foraminifera ρ ($r = -0.53$) and TIC ($r = -0.65$).

5.4.5 Biomarkers

GC-MS analysis of lipid extracts on the aliphatic portion of 42 samples of the El Pujal section reveals *n*-alkanes (m/z 57) with a bimodal distribution, showing two maxima, one that covers $\leq nC_{17}$ and another one at $\geq nC_{19}$ with a minimum between

Figure 5-8 Stratigraphic position and *n*-alkanes distribution of 12 of the 42 samples analyzed for biomarkers. Black colored bar graphs represent the *n*-alkanes distribution of samples along intervals enriched in TOC (argillaceous limestone and marlstone layers) and the green colored bar graphs represent intervals depleted in TOC (limestone layers).

pristane (Pr) and phytane (Ph) (Fig. 5-8). The aliphatic fraction in all chromatograms is dominated primarily by *n*-alkanes and acyclic isoprenoids. The *n*-alkanes show a distribution ranging from *n*C₁₀ to a maximum of *n*C₃₁ in all the analyzed samples, with no difference in carbon chain length between limestone, argillaceous limestone, or marlstone intervals (Fig. 5-8). CPI calculated from the longer chain *n*-alkanes (*n*C₂₅-*n*C₃₄) is used here as a maturity index (refer to methods), with values that average 1.41 for the entire

section with no particular stratigraphic pattern. Since there is no difference in the carbon chain length of samples throughout the section, TAR ratios were calculated (refer to methods). TAR values average 0.23 and display a remarkable trend whereby they drop below the average in argillaceous limestone and marlstone beds, while the values rise above the average in the limestone layers (Fig. 5-9A). Other biomarker parameters such as the ACL of leaf wax components (nC_{25} - nC_{33}) commonly used as a proxy to determine the type of terrestrial vegetation, as well as for deducing climatic conditions on land (refer to methods), were also calculated. The ACL of El Pujal section yields values from 26.02 to 27.23, with an average of 26.88 (Fig. 5-9C; Appendix 5C) and shows a negative

Figure 5-9 (A-B-C-D) Stratigraphic correlation between lithology and various organic geochemical parameters. Gray bars correspond with intervals of argillaceous limestone and marlstone deposition. (E) Log-log cross-plot of Pr/nC_{17} vs Ph/nC_{18} for all 42 analyzed samples. Notice that in general the samples plot within the mixed type II/III kerogen with only a few plotting below in the marine type II kerogen zone.

correlation to TOC ($r = -0.53$), whereby the lower values correspond to argillaceous limestone and marlstone intervals.

5.5 Discussion

5.5.1 Stable Carbon Isotope and Biostratigraphic Correlations

Coeval variations in stable carbon isotope ($\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$) profiles of Cretaceous pelagic and shallow water deposits are generally regarded as reflecting

perturbations in the global carbon cycle (Scholle and Arthur, 1980; Arthur et al., 1987; Schlanger et al., 1987; Weissert, 1989; Jenkyns, 1995; Leckie et al., 2002; Weissert and Erba, 2004; Tejada et al., 2009). Hence, the concordance in the $\delta^{13}\text{C}$ pattern of widely distributed Barremian-Aptian sections has become the hallmark of this interval of the Lower Cretaceous and attests to the utility of this proxy as a correlation tool, especially when corroborated by biostratigraphic markers and magnetostratigraphy (Gale et al., 1993; Moullade et al., 1998; Kuhnt et al., 1998; de Gea et al., 2003; Erba, 2004; Najarro et al., 2011; Moullade et al., 2015; Erba et al., 2015). Specifically, based on the similar pattern registered in various Barremian – Aptian sites, Menegatti et al. (1998) introduced a temporal subdivision of the $\delta^{13}\text{C}$ curve into segments labeled C1-C8 that have been calibrated with index fossils and now serve as a standard for correlating Lower Cretaceous sections (e.g. Kuhnt et al., 1998; Erba, 2004; Millán et al., 2009; Stein et al., 2012; Papp et al., 2013; Sanchez-Hernandez and Maurrasse, 2014; Phelps et al., 2015; Scott, 2016). Although regional modulating factors such as the source of OM, biological fractionation, and degree of thermal maturation, and/or diagenesis, can affect the original isotopic signal, most sites record concurrent $\delta^{13}\text{C}$ signatures (e.g. Menegatti et al., 1998; Godet et al., 2014; Sanchez-Hernandez and Maurrasse, 2016). Here we use the established constancy of the Aptian $\delta^{13}\text{C}_{\text{org}}$ curve to correlate the El Pujal sequence with other well-studied Tethyan realm sections (Fig. 5-10), namely Roter Sattel, Cismon and the El Pui section (Menegatti et al., 1998; Sanchez-Hernandez and Maurrasse, 2016).

A detailed examination of the $\delta^{13}\text{C}_{\text{org}}$ trend for segment C5 at Roter Sattel shows that the values start at $\sim -25\text{‰}$ and then take a negative dip to $\sim -25.2\text{‰}$ at ~ 5.125 m. Upwards, the values stay relatively stable with an approximate average of -25.2‰ up to

Figure 5-10 Chemostratigraphic correlation based on $\delta^{13}\text{C}_{\text{org}}$ of the El Pujal section with other Tethyan sections. The C segments correspond to the $\delta^{13}\text{C}$ subdivisions proposed by Menegatti et al. (1998). Area shaded in gray corresponds to the interval covering OAE1a in each respective section. (E) Plot of El Pui and El Pujal with identical vertical and horizontal scales. The yellow star marks the highest value within segment C5 and corresponds to equivalent points in each section. The purple dashed line shows the interval corresponding to segment C5.

5.5 m where they take a positive shift to $\sim -24.9\text{‰}$ (Fig. 5-10A, point marked with a star) followed by a decrease past -25.6‰ , marking the end of C5 and the assigned beginning of segment C6. Similarly, the carbon isotope trend in the $\delta^{13}\text{C}_{\text{org}}$ record of the Cismon section shows segment C5 starting with a value of $\sim -25.8\text{‰}$, but gradually decreasing to $\sim -26\text{‰}$ at 265.25 m, succeeded by a series of positive and negative variations culminating in the most positive value (-23.6‰) recorded for segment C5 at 263.375 m (Fig. 5-10B, point marked with a star). A negative excursion ensues to just below -25.2‰ , designated as the end of C5/beginning of segment C6.

By comparison, at El Pui, segment C5 begins at 212 m (Fig. 5-10C) with a value of -23.68‰ and decreases to -24.32‰ , succeeded by a series of positive and negative variations ending at a value of -24.62‰ at 228.80 m (interval of ~ 16.8 m). Above that interval, the $\delta^{13}\text{C}_{\text{org}}$ values take a positive shift reaching up to -22.63‰ within the last samples analyzed at that site (Sanchez-Hernandez and Maurrasse, 2016). In the absence of further samples, these authors indicated that the rise to positive values implied the onset of segment C6 at the end of the studied El Pui section. To establish the continuity of the chemostratigraphic data between the El Pui and El Pujal sections we first used the physical correlation of the beds. Because the beds that compose the homoclinal structure of the asymmetric Santa Fè syncline are clearly visible and undisturbed (García-Senz, 2002; Sanchez-Hernandez and Maurrasse, 2014), thus it was possible to use their strike to project their continuity farther east across the south side of the Cabo valley and ensure correlation with the El Pujal site (Fig. 5-1). Based on this continuity the projected beds from each other side of the valley provide an initial physical correlation and coupling of

the two sites to form a continuous composite section that further extend the study of lower Aptian sedimentary deposits of the Organyà Basin (Fig. 5-2).

The lithologic correlation is confirmed by the carbon isotope results which yield values at the base of the El Pujal section starting with a $\delta^{13}\text{C}_{\text{org}}$ of -22.59‰, consistent with the El Pui section where the terminal value recorded in sample C12-480 is -22.76‰ (Fig. 5-10D, E, point marked with a star). Unlike the conventional segment C6, however, this initial positive shift recorded at El Pui coinciding with the value at El Pujal does not maintain its rise. Instead, the $\delta^{13}\text{C}_{\text{org}}$ values decrease shortly thereafter to -24.23‰ (Fig. 5-10D, point marked with a star), and continue upwards with a more negative trend hovering around an average of $\sim -23.40\text{‰}$ (Fig. 5-10E). By comparison, we may deduce that the slight positive shift observed in the extended sequence of the Organyà sediments thus forms a short-lived spike comparable to the more condensed Roter Sattel and Cismon sections shown in Figure 5-10A, B, and marked with a star. Hence, we consider the $\delta^{13}\text{C}_{\text{org}}$ values recorded at the end of the El Pui section and the base of the El Pujal section to be equivalent to the highest values for segment C5 at Roter Sattel and Cismon (Fig. 5-10A, B, point marked with a star). While there is an overall similar trend for segment C5 in all of these sections, there are distinct differences in amplitude between them. Such discrepancies are well known in the chemostratigraphic record because of the different factors such as, provenance of OM and diagenesis that may affect the actual isotopic values. In fact, because of these modulating factors such unequal variations are not exclusive to the lower Aptian sections, similar cases have been reported for coeval carbon isotope curves elsewhere at either older (e.g. Sandoval et al., 2012) or younger stratigraphic levels (Schouten et al., 2007). In the latter case that addresses the Paleocene-

Eocene thermal maximum (PETM) CIEs the carbon isotopic values show magnitudes with a difference as large as 6.5‰ between diverse marine sites worldwide (see Table 1 in Schouten, et al., 2007). Although the driver of these discrepancies is poorly constrained and may be unique to each basin, since the sediments in the El Pujal section have Pr/Phy ratios <2, we may rule out an overmature state as a factor affecting the carbon isotope values (ten Haven et al., 1987, 1988; Powell, 1988; Sanchez-Hernandez et al., 2014). Of special importance in the El Pujal section is the obvious contribution of terrestrially-derived organic matter (Fig. 5-8; also, see discussion of biomarkers below) which may be part of the local factors, because of the possible effects of carbon isotope fractionation specific to photosynthetic pathways (O’Leary, 1988) associated with the types of extant vegetation that contributed organic remains to the Organyà Basin. Indeed, a clear difference between C3 plants (average $\delta^{13}\text{C}_{\text{org}} \sim -27\text{‰}/-28\text{‰}$), as compared to C4 plants (average $\delta^{13}\text{C}_{\text{org}} \sim -13\text{‰}$) is well demonstrated (O’Leary, 1988). Clearly, the magnitude of the positive inflection suggests forcing mechanisms related to local sources of organic matter. Given that variations in physiological traits that may cause wide range of carbon isotope values (e.g. Ehleringer et al., 1993) in the extant vegetation are yet unknown, further work is necessary to resolve such relationship and fully understand their effects on the actual regional amplitude of these shifts.

With the evidence at hand, we propose that the apparent carbon isotope positive shift in the carbon isotope C5 of the extended Organyà succession is a minor episode within that segment because the succeeding values continue toward a negative trend (Fig. 5-10E). Thus, the El Pujal section further documents carbon isotopic variations in segment C5, as previously reported in preceding segments of the El Pui section due to the

high bulk accumulation rate in the basin (García-Senz, 2002; Sanchez-Hernandez et al., 2014).

The micropaleontological associations at El Pujal give further credence to the chemostratigraphic correlation because petrographic analysis and results from selected disaggregated samples show that hedbergellids (Fig. 5-5C5, C6, C7, C17, C18) are the most common planktonic foraminifers in this interval, accompanied by rare to common globigerinelloids and *Leupoldina cf. cabri*. Since *L. cabri* is recorded at 13.77 m and its biozone is within OAE1a (Erba, 1994; Moullade et al., 1998; Cobianchi et al., 1999; Erba et al., 1999; Bellanca et al., 2002; Verga and Premoli Silva 2002; Erba, 2004; Coccioni et al., 2004; Heldt et al., 2008; Moullade et al., 2015) its presence further corroborates the $\delta^{13}\text{C}_{\text{org}}$ results that permit to position the basal part of the studied El Pujal section within the event interval correlative with carbon isotope segment C5.

5.5.2 Accumulation Rate and the Extent of the Carbon Isotope Segments in Different Sections

The high-resolution carbon isotope curve of the studied El Pujal section provides greater detail of the temporal variations because of its extended thickness that reflects a much greater accumulation rate in the Organyà Basin as compared to other Tethyan localities (García-Senz, 2002; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2016). By comparison, the Selli level (OAE1a) in the Cismon Apticore site extends over ~ 5.11 m (18.77 m to 23.68 m; Erba et al., 1999). If we apply the estimated durations of ~1 Ma (Larson and Erba, 1999) to a maximum of ~1,271 ky (Li et al., 2008; Scott, 2016) for OAE1a, they yield an estimated mass accumulation rate at the Cismon Apticore site of ~ 0.50 cm Ky⁻¹ maximum, for the entire event. In contrast, the interval

C3 – C5 (only partial C5) in the adjacent El Pui section of the Organyà Basin comprises at least ~ 66 m (C3 = 36 m; C4 = 13 m; partial C5 = 17 m) (Sanchez-Hernandez and Maurrasse, 2016). Based on the overall maximum suggested duration of 1,271 Ky at Cismon, Italy (Table 2, in Li et al., 2008), our estimate for the dry bulk accumulation rate of the three segments at El Pui is ~ 5.19 cm Ky⁻¹ (66 m ÷ 1, 271 ky), which is in agreement with previous estimates (Sanchez-Hernandez and Maurrasse, 2016). Taking account of the variability in the accumulation rates of segments C2 to C4 reported by these authors, here we forgo to estimate a specific rate for C5 alone because its magnitude is not fully constrained as the study of the upper part of the El Pujal section is ongoing. Nonetheless, such high mass accumulation rate in the Organyà Basin may foretell a greater detailed record of minor temporal changes in the succession. The high mass accumulation rate recorded in the El Pujal section asserts the instability of the adjacent land masses at that time and is comparable to active tectonic areas where such high values are reported in coeval Cretaceous forearc basin sediments, as for instance the Yezo Group exposed in Hokkaido, northern Japan where dry bulk accumulation rates may exceed ~ 11 cm Ky⁻¹ (Takashima et al., 2004).

5.5.3 Biomarker Interpretation: Source of Organic Matter, Thermal Maturation

Biomarker analysis of the El Pujal section (Fig. 5-8) yielded *n*-alkanes distribution ranging from *n*C₁₀ to a maximum of *n*C₃₁ revealing two maxima that include shorter chain lengths at $\geq nC_{19}$ and longer chain lengths at $\geq nC_{19}$ with a minimum between pristane (Pr) and phytane(Ph). Different sources of higher plants (C3 trees, C4 grasses) may contribute to observed short chain *n*-alkanes in modern sediments (e.g. Kuhn et al., 2010), nonetheless previous studies have demonstrated that lipid extracts derived from marine

planktonic organisms and or bacterial sources have a recognizable enrichment in shorter chain *n*-alkanes ($\leq nC_{19}$), in particular those with odd-number of carbons (nC_{15} , nC_{17} , nC_{19}) (Forster et al., 2004; Peters et al., 2005). Conversely, aquatic macrophytes from both marine and non-marine environments show an enrichment in the mid-chain length region (nC_{20} - nC_{25}), while terrestrial vegetation shows higher proportions of longer chain *n*-alkanes ($>nC_{25}$), especially in the longer odd-numbered homologues (nC_{27} , nC_{29} , nC_{31}) (Cranwell, 1982; 1984; Ficken et al., 2000; Mead et al., 2005; Feakins et al., 2007; Kuhn et al., 2010). Thus, the aliphatic fraction of lipid extracts from the El Pujal section sediments reveals *n*-alkanes that represent a mixed source of OM in the basin (Fig. 5-8).

The carbon preference index (CPI) is a proxy used mainly to determine the degree of thermal maturation of ancient sediments and relies on the observation that lipids derived from terrestrial OM display a predominance of odd-over even-carbon (OEP) number of long chain *n*-alkanes (nC_{25} - nC_{34}) (e.g. Bray and Evans., 1961; Kuhn et al., 2010). Although this predominance can be affected by a number of variables, such as climatic conditions, source of longer chain *n*-alkanes and biodegradation, the CPI indicative of low maturity and predominantly terrestrially derived OM should result in a high value (>1), whereas when it decreases and approaches 1 it should correspond to higher levels of maturation (Bray and Evans., 1961). The calculated CPI of the longer chain homologues in the El Pujal sediments is relatively low (1.41), suggesting some degree of thermal maturity. However, the total ion chromatogram throughout the section shows the concurrence of low molecular weight *n*-alkanes ($<C_{13}$) with longer molecular constituents in a bimodal distribution associated with a very low hump of unresolved compounds (UCM) (Fig. 5-8), which indicates that the *n*-alkanes distribution is authentic

with little to no thermal alteration, in agreement with previous studies based on Pr/Ph ratios (Sanchez-Hernandez and Maurrasse, 2016).

The terrestrial aquatic ratios (TAR) were calculated to further aid in the interpretation of the *n*-alkanes and determine the contribution of terrestrial vegetation relative to *in-situ* production of the total OM. Analysis of the data shows that TAR values remain consistently low with an average of about 0.23, but with distinct differences between intervals enriched and those depleted in TOC, respectively (Fig. 5-9A). The mean TAR suggests noticeable contribution of terrestrial OM, and the values vary along with a trend similar to fluctuations associated with lithologies observed in multiple characteristic geochemical components and benthic foraminifers shown in Figures 5-5, 5-6 and 5-7, respectively. However, in contrast to expected results, TAR values dip below the average (0.19, 0.15, 0.05, 0.17, 0.21, 0.18) in concordance with these respective levels of increased terrigenous materials (1.47 m, 3.68 m, 5.82 m, 7.67 m, 9.78 m, 12.2 m). Temporal correlation with the different parameters analyzed shows that on the overall, these minimum TAR values reveal an inverse trend relative to RSTEs, TOC ($r = -0.52$) and major elements, but a positive correlation with TIC ($r = 0.52$) and benthic foraminifera ρ ($r = 0.41$). This discrepancy may be explained by the dilution effect of enhanced *in-situ* primary productivity that increased the input of OM from shorter chain *n*-alkanes relative to the land-derived longer chain *n*-alkanes. As the distribution patterns of major and trace elements reveal (Fig. 5-6; Fig. 5-7), these intervals characterize higher input of biolimiting nutrients (Fe, P) into the basin that heightened productivity, thereby decreasing the TAR values. To help illustrate this dilution effect, a plot (Fig. 5-9B) of the inverse TAR (terrestrial/marine) marine/terrestrial (nC_{17}/nC_{31}) results in a positive

correlation with TOC ($r = 0.58$), major terrestrially derived elements, RSTEs, but a negative correlation with TIC ($r = -0.47$) and benthic foraminifera ρ ($r = -0.41$).

The average chain length (ACL) of *n*-alkanes (nC_{25} - nC_{33}) based on the abundance of the odd numbered carbon chain (Poynter and Eglinton, 1990) of terrestrial *n*-alkanes is used primarily in sediments to distinguish the source vegetation producing them (Jansen et al., 2010; Carr et al., 2010; Diefendorf and Freimuth, 2017) and climatic conditions of adjacent land masses (e.g. Feakins et al., 2007). As observed for the parameters discussed previously, the ACL of the leaf wax components in the El Pujal sediments also varies with the lithologic facies (Fig. 5-9C) and ranges from 26.02 to 27.23, with an average of 26.88. Notably, there is a moderate negative correlation ($r = -0.53$) between TOC and ACL, whereby intervals of higher TOC (Fig. 5-8) are more strongly influenced by the lower range of the ACL parameter or *n*-alkanes derived from terrestrial plants which would be more enriched in nC_{26} . This close compatibility suggests that the source of the longer homologues is derived from woodland vegetation, and also points towards wetter conditions during the deposition of argillaceous limestone and marlstone intervals.

The pristane (C19)-phytane (C20) (Pr/Ph) ratios have been used as means of deducing the redox conditions during deposition. This is based on the knowledge that these acyclic isoprenoids are derived from degradation of the phytol side chain of chlorophyll a and b molecules which during reducing conditions leads to the formation of phytane, whereas under oxidizing conditions pristane is preferentially synthesized (e.g. Brooks et al., 1969; Didyk et al., 1978). Therefore, the values taken as useful metric for assessing depositional redox conditions suggested ratios of Pr/Ph <1 to indicate anoxic conditions, while ratios >1 would imply oxic environments (Powell and Mckirdy 1973;

Didyk et al., 1978). However, some ambiguity may arise because the pristane-phytane ratios may increase with increasing terrigenous contributions (Rashid, 1979), and other biomolecules can serve as precursors to pristane and / or phytane through mechanisms that are independent of redox conditions. Some examples include unsaturated isoprenoids derived from zooplanktons (Blumer and Snyder, 1965), tocopherols derived from plants (Goossens et al., 1984), and archaebacterial glycerol ether lipids especially in the presence of clay minerals (Navale, 1994). The Pr/Ph ratios in the El Pujal section are consistently >1 (Appendix 5C) averaging ~1.81 and show a weak negative correlation ($r = -0.13$) with TOC and RSTEs (Appendix 5A, 5C), thus suggesting that extant depositional redox conditions might not be the major factors that affected the Pr/Ph origin. Given the mix character of the OM (Fig. 5-8), a combination of factors might have been involved, including OM source, which will need further explicit data from other geochemical redox proxies (Peters et al., 2007).

Figure 5-9E illustrates our use of the values of Pr/ n C₁₇ and Ph/ n C₁₈ (Lijmbach, 1975; Shanmugam, 1985) as source indicators to determine the potential type of kerogen (II, III) present in the section. Since the Pr/Ph ratios are predominately below the threshold (>2.5) (ten Haven et al., 1987, 1988; Powell, 1988), therefore thermal overmaturity can be ruled out as a possible factor to decrease these values. Although biodegradation could have also increased these values because bacteria preferentially degrade the more labile *n*-alkanes over the isoprenoids, but the lack of evidence of any such factor supports the assertion that the values obtained yield representative results. Pr/ n C₁₇ shows consistently low values with an average of 0.35. Similarly, Ph/ n C₁₈ are also low with an average value of 0.21. Log-log cross-plots of Pr/ n C₁₇ vs Ph/ n C₁₈

indicates a mixed source of OM with most samples plotting in the type II-III kerogen mixture zone, corroborating previous results from biomarkers, TAR and extracted ion (m/z 57) *n*-alkanes distributions, which also suggest a mixture of algal and terrestrial OM (Fig. 5-9E).

5.5.4 Evidence of Episodic Dysoxia and its Role in OM Preservation

Chemostratigraphic records showing high abundance and depletion of different redox sensitive trace metals (RSTEs) are widely corroborated to provide helpful metric for the assessment of redox conditions of modern and paleo-depositional systems (e.g. Brumsack, 1980, 2006; Calvert and Pederson, 1993; Dean, 1999; Yarincik et al., 2000; Tribovillard et al., 2004; Pattan and Pearce, 2009; Sanchez-Hernandez and Maurrasse, 2014; 2016). The general consensus discussed in the literature recognizes that under reducing conditions RSTEs such as V, Ni, Co, Cr, Cu, Mo may become enriched in sediments through different reactive pathways: formation of organometallic complexes, precipitation as oxides and hydroxides, adsorption on organic surfaces, or by forming insoluble sulfides (e.g. Tribovillard et al., 2004 ; Bodin et al 2007).

Because of various alternative deliveries of these elements to the ocean via continental overflow and the nature of adjacent source rocks the values of relative high abundance of RSTEs alone may not provide enough evidence asserting oxygen deprived conditions. Accordingly, mindful of conflicting results that may arise with the use of these paleoredox proxies (Rimmer, 2004; Xu et al., 2012; Sanchez-Hernandez and Maurrasse, 2014), we used complementary co-factors to further validate potential oxygen deficient conditions. Hence, here we also use the combination of other oxygenation proxies (TOC, benthic foraminifera ρ , pyrite concentration, bioturbation index), in

concert with Σ RSTEs EI to approximately characterize oxygen conditions during sedimentation.

We used elemental ratios of thorium and uranium (Th/U) in an effort to add additional supporting evidence to assess redox conditions, because previous studies have successfully relied on this elemental ratio as a proxy to explain anoxic deposition of sediments (Wignall and Twitchett, 1996). This redox proxy is based on the fact that Th only has one redox state (IV), hence its concentration in sediments is unrelated to redox conditions (Hazen et al., 2009). In contrast, dissolved U(VI) is removed from oxidizing seawater to reducing sediments as insoluble U(IV) by various biogeochemical processes (Langmuir, 1978; Anderson et al., 1989; Yamada and Tsunogai, 1984; Calvert and Pedersen, 1993; Bura-Nakić et al., 2018). In the reduced state U removal includes uranous fluoride complexes, organometallic complexes with humic acids and particulate organic matter, or through the direct precipitation as uraninite (UO₂) (Anderson et al., 1989; Klinkhammer and Palmer, 1991; Zheng et al., 2002). Consequently, a decrease of oxygen during deposition reduces the concentration of soluble U(VI) in the water column, hence the resulting depletion of U in seawater is reflected in the increased concentration of U in sediments deposited during this time. Therefore, this parameter should be representative of redox conditions and should thus show lower Th/U values during intervals of oxygen deprived conditions. However, Th/U ratios in the sequence at El Pujal fall afield of the expected theoretical assumption because higher values correlate with organic-rich layers that yield lower concentration of benthic fauna (Fig. 5-5B), lower bioturbation index, higher pyrite concentration, significant enrichments in RSTEs, and Σ RSTEs EI well above the background average (Fig. 5-7). Thus, Th is relatively

enriched within these intervals even though the basin was evidently experiencing episodic oxygen-deficient conditions, a process that should have enriched U instead. As neither of the accepted conventional biogeochemical processes could resolve this apparent discrepancy, an understanding of the regional paleogeography with regards to the provenance of the terrigenous materials (Sanchez-Hernandez et al., 2014) provides a helpful explanation in relation to the extant crystalline terranes that constituted the watersheds adjacent to the basin. The Pyrenees include pre-Variscan (Ordovician) and Variscan (Late Paleozoic/ Carboniferous) crystalline terranes with granitoid plutons (Ábalos et al., 2002; Denèle et al., 2014) ranging in size from a few km² to over 100 km², and regions of high grade mica schists and migmatites (Boulvais et al., 2007; Poujol et al., 2010; Olivier et al., 2016). These crystalline terranes also incorporate large bodies of orthogneiss (Barbey et al., 2001; Cocherie et al., 2005; Castiñeiras et al., 2008; Denèle et al., 2009; Navidad et al., 2010; Castiñeiras et al., 2011; Liesa et al., 2011) and are coeval with comparable rocks found in Galicia, northwest area of the Iberian Peninsula, known as the Galiñeiro Igneous Complex. This crystalline complex is of particular interest because it contains significant enrichments in REE and high field strength elements (HFSE), especially Th which reaches values as high as 4923 ppm in orthogneisses (Montero, 1993; Montero et al., 1998; 2009). Comparatively the Pyrenean correlative tends to have lower Th concentrations with values rarely exceeding 1000 ppm (Castiñeiras et al., 2011), but other available sources which consist of differentiated crystalline rocks that include monazite (Ce, La, Nd, Th) (PO₄, SiO₄) may also be recognized as potential contributors to the relatively high Th concentrations in the Organyà Basin (Fig. 5-7; Appendix 5B). Magmatic differentiation and/or partial melting

of the crust may have induced monazite fractionation in the Variscan granites and migmatites, as this process leads to concentration of rare-earth elements (REE) and Th in various accessory minerals (Miller and Mittlefehldt, 1982; Weber et al., 1985; Maruéjol et al., 1990; Ditz et al., 1990; Schandl and Gorton, 2004; Boulvais et al., 2007). Relatively high concentration of Th (up to 12 wt%) is found mainly with the rare-earth phosphate phases, monazite and xenotime (YPO_4) (Wark and Miller, 1993). Monazite containing relatively low Th (rarely exceeding 1 wt%) also occurs with abundant albitites produced during extensive magmatic hydrothermal metasomatism throughout the Pyrenees (Clavières, 1990; Ditz et al., 1990; Ayers et al., 1999; Spear and Pyle, 2002; Schandl and Gorton, 2004; Boulvais et al., 2007; Poujol et al., 2010; Grand'Homme, 2016). The regional geologic record of rocks adjacent to the Organyà Basin thus provides a robust evidence that helps to clarify the surprisingly high Th in sediments of the El Pujal section despite lacking anoxia. In fact, the excellent correlation of Th with P ($r = 0.77$) further lends support to our assertion that intervals of higher Th/U in the El Pujal sequence document periods of enhanced terrigenous riverine fluxes that delivered detrital Th to the basin comparable to previous discussions assessing the provenance of P in the Organyà Basin (Sanchez-Hernandez and Maurrasse, 2014; Sanchez-Hernandez et al., 2014). Our results underscore the need to also consider conterminous terranes when using Th/U ratios, because the relationship between these two elements might not be as simply influenced by the redox conditions within the basin.

5.5.5 Water Column Oxygenation

The sedimentary record of the El Pujal section correlated with carbon isotope segment C5 shows no distinctive lithologic changes with pronounced increase in TOC

reflective of anoxic conditions as documented with the continuous development of OAE1a in most locations worldwide. Nevertheless, our data indicate that the perturbation of the global carbon reservoir characteristic of the event was essentially reflected in the overall isotopic composition of the Organyà Basin. Arguably, the six intermittent intervals characterized by increase in Σ RSTEs EI, slightly laminated organic-rich layers coincident with lower concentration of benthic fauna, lower bioturbation index, and higher pyrite concentration imply that oxygen-deficient conditions recurred intermittently during these times. Complete anoxic conditions can be ruled out because of the persistence of a few benthic foraminifera taxa, including both infauna and epifauna morphotypes (Jorissen et al., 1995; Jorissen, 1999), throughout the different layers. Variation of the benthic fauna indicates that oxygen may have decreased to sensitive level at the sediment water interface, but the water column never reached anoxic levels (Wignall and Myers, 1988; Tyson and Pearson, 1991, Murray, 2001; Meyer and Kump, 2008). Temporal variations in the distribution patterns of RSTEs and the other oxygen proxies throughout the studied section further characterize fluctuating conditions in the basin as the limestone layers indicate higher ventilation of the water column. The results of the El Pujal section further corroborate previous studies that determined mainly intermittent dysoxic and oxic conditions in the progression of OAE1a in the Organyà Basin (Sanchez-Hernandez and Maurrasse, 2014; Sanchez-Hernandez et al., 2014). Similar records have been documented in pelagic and hemipelagic deposits from the Tethys, northern and southern Atlantic and the Pacific from the Hauterivian up to the Aptian (Weissert et al., 1979, 1985; Koutsoukos et al., 1991b; Mutterlose and Ruffell, 1999; Bersezio et al., 2002, Heldt et al., 2008; Sanchez-Hernandez and Maurrasse, 2016).

Perhaps, the recurrent pattern recorded in the sediment conveys respective modulating local factors that may obscure possible orbital effects that are yet to be determined.

5.5.6 Productivity and Water Column Stratification as Driving Factors in OM Preservation

As sediments of the El Pujal section show punctuated peaks of enhanced OM abundance, interrelated *n*-alkanes document their origin from a mixture of *in-situ* and terrestrially-derived photosynthetic producers (Fig. 5-8). In addition to the concurrence of these levels with increased abundance of environmentally characteristic trace metals (Fig. 5-7), the fluctuations further show a striking pattern of synchronicity with peaks in P and Fe (Fig. 5-6), which are critical biolimiting elements to sustain organic productivity (DNA, RNA, polypeptides, ATP, phospholipids, proteins, photosynthesis) (Hart, 1934; Rueter and Ades, 1987; Martin and Fitzwater, 1988; Krom et al., 1991; Geider and La Roche, 1994; Kumar et al., 1995; Zohary and Robarts, 1998; Tyrrell, 1999; Benitez-Nelson, 2000; Boyd et al., 2000; Diaz et al., 2001; Gervais et al., 2002; Coale et al., 2004; Paytan and McLaughlin, 2007; Falkowski and Raven, 2007; Blain et al., 2007). Since the respective roles of P and Fe are well established as critical in the marine biogeochemical cycle of primary producers and heterotrophic communities in modern oceans (e.g. Popendorf and Duhamel, 2015), variations recorded in the El Pujal sediments may be interpreted as archives of similar ecosystem relationships in the Organyà Basin. Indeed, our environmental interpretation relies on known delivery pathways of P and Fe to organisms in the ocean because they derive essentially from land areas (e.g. Kumar et al., 1995). Recycling of P occurs in the upwelling and oligotrophic environments of the ocean via remineralization within a complex pool of dissolved organic phosphate (DOP),

dissolved inorganic phosphate (DIP), and mostly as tri-Phosphate ions that sustain the cycle of productivity. In the semi-restricted Organyà Basin the absence of biogenic silica (Sanchez-Hernandez and Maurrasse, 2016) implies lack of upwelling, therefore sustained productivity depended permanently on riverine input of P. The correlative abundance of terrestrially-derived elements (Si, Al, Ti) during intervals of OM sequestration (Fig. 5-6) provides supportive evidence relating increased riverine fluxes that simultaneously supplied biolimiting nutrients (P and Fe), and other terrestrial matters incorporating allochthonous OM (Fig. 5-8), as attest the biomarker composition correlated with these OM spikes (Fig. 5-8). The effect of abundant influx of less dense freshwater would have also led to water column stratification lacking ventilation, analogous to the modern day Black Sea (Özsoy and Ünlüata, 1997; Giosan et al., 2012) and discussed for the early stages of OAE1a in the basin (Sanchez-Hernandez and Maurrasse, 2016).

In essence, the data in the lower portion of the El Pujal section suggest that the combined effect of periodic increase of riverine fluxes delivering biolimiting P and Fe enhanced export production together with water column stratification. It ensued that recurring maximum biological oxygen demand (BOD) in the water column exacerbated oxygen deficiency that heightened OM preservation in the basin. Higher Al content at these levels (Fig. 5-6) interpreted as derived from clays (Eslinger and Pevear, 1988) and previously documented in the basin (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2016) further supports this assumption. In addition to essential productivity factors and hydrodynamic conditions involved in OM production and preservation in the Organyà Basin, the increase in clays most likely functioned as protective agents of the OM either through sorption, or through physical encapsulation

preventing it from remineralization by microbial exoenzymes (Mayer, 1994; Keil et al., 1994; Hedges and Keil, 1995; Ransom et al., 1997; Keil and Cowie, 1999; Satterberg et al., 2003; Kennedy et al., 2002, 2014).

Since the various proxy data provide concurrence of continuous open marine environmental conditions in the basin punctuated by episodes of increased freshwater input, the pattern suggests the effects of regional climate variability. Accordingly, increased hydrologic conditions on land were related to much wetter conditions during these intervals. The presence of smaller values in ACL of the leaf wax components (nC_{25} - nC_{33}) from terrestrially derived vegetation lends support to this interpretation.

5.5.7 Principal Component Analysis and Paleoecologic Interpretation

To further shed light on the main variables controlling OM sequestration and its paleoenvironmental significance, principal component analysis (PCA) was conducted on 17 variables (TIC, TOC, Si, Al, Ti, Fe, P, V, Cr, Co, Ni, Cu, Mo, Th/U, benthic foraminifera ρ , TAR, ACL). The analysis permitted the separation of the samples into 3 clusters that coincide with the three identified lithologies (Cluster I = Limestones; Cluster II = Argillaceous Limestones; Cluster III = Marlstones (Fig. 5-11). The first principal component (PC1) accounts for 67.42% of the variance, with most variables showing strong loadings except for Th/U (0.17) and benthic foraminifera ρ (-0.17). Principal component 2 (PC2) accounts for 11.33% of the variance with TIC, Th/U, Mo, Ni and benthic foraminifera ρ showing the strongest loadings (Scores and Loadings summarized in Appendix 5D). Samples plotting along PC1 with high positive scores correspond with intervals showing higher values of TOC, terrestrial matter, biolimiting nutrients, and RSTEs, whereas samples with strong negative scores correspond with high values of TIC,

Figure 5-11 Results from PCA based on 17 combined variables. Notice how the samples separate into distinct lithologic groups.

foraminifera ρ , TAR and ACL. High positive scores along PC1 are therefore interpreted as intervals of highest dysoxia consistent with wetter periods (smallest ACL) delivering increased volumes of riverine water containing highest Si, Al, Ti, and biolimiting nutrients (P, Fe). PC1 represents more extreme variability from oxic/oligotrophic/dry to dysoxic/eutrophic/wet. High negative scores along PC1 are interpreted as dryer periods with less freshwater input, more oligotrophic conditions and higher oxygen content. The strongest positive loadings along PC2 belong to TIC, Mo, Ni and foraminifera ρ , while strong negative loadings belong to Th/U, Si and ACL. Samples plotting along PC2 with high positive scores are mostly associated with high carbonate content and more oxic depositional environment. A noteworthy contrast however, is that all RSTEs in PC1 have an inverse loading trend to TIC, but some RSTEs, especially Ni and Mo, show a positive loading trend with TIC. Samples with high negative scores plotting along PC2 have a stronger siliciclastic and dysoxic signature, therefore PC2 is interpreted to represent the transition carbonate/oxic to siliciclastic/dysoxic trend.

5.5.8 Depositional Model of the Organyà Basin during Segment C5 of OAE1a

Based on the results discussed for the El Pujal section, delivery of terrigenous elements into the Organyà Basin was the primary modulating factor superimposed on the overall extant global conditions associated with OAE1a. Watershed forcing can be inferred to have been driven by the paleophysiographic setting of a semi-restricted basin influenced by landmasses of crystalline terranes (Barbey et al., 2001; García-Senz, 2002; García-Alcade et al., 2002; Ábalos et al., 2002) coupled with a paleolatitude of approximately 25° to 30° north of the Equator under humid tropical climatic conditions (Molina and Salas, 1993; Salas et al., 1995; Barron et al., 1995; Masse et al., 2000;

García-Senz, 2002; Yuste et al., 2017). We propose that continuous evolution of environmental conditions during segment C5 of OAE1a in the Organyà Basin were fairly analogous to those recorded in the modern-day Black Sea (Özsoy and Ünlüata, 1997; Giosan et al., 2012), or the eastern Mediterranean (e.g. Wu et al., 2018). Likewise, the lithofacies in the El Pujal section extend the trend in the subjacent hemiplegic facies of the El Pui section (Sanchez-Hernandez and Maurrasse, 2014; 2016; Sanchez-Hernandez et al., 2014) and presumably reflect regional climatic effects of insolation-driven fresh water forcing of continental runoff as demonstrated in the Mediterranean area for similar cycles (Wu et al., 2018), and as characterized in the following models (Fig. 5-12A, B, C):

1. Fig. 5-12A. Continuous riverine fluxes in the basin supplied Fe and P likely derived from the weathering of apatite-bearing Variscan crystalline terranes in the watershed areas (García-Alcade et al., 2002; Ábalos et al., 2002; Sanchez-Hernandez et al., 2014) that sustained productivity under mesotrophic conditions. These times were correlative with sedimentation associated with some degree of mixing because of weakly stratified water column.
2. Fig. 5-12B. The results suggest periodic riverine increases as indicated by greater abundance of major elements RSTEs associated with increased TOC and diminished density of benthic fauna signal relatively higher fluvial loads creating a stronger density gradient in the water column together with heightened export production leading to further oxygen deficient conditions recorded at these levels.
3. Fig. 5-12C. The lowest values of ACL in the two marlstones denote more pronounced shifts toward wetter climatic conditions on land, and highest Si, Al, Ti, P and Fe values provide evidence of largest increase in the input of riverine fluxes into

the basin. In addition, greatest abundance of TOC, RSTEs that coincide with the lowest densities in benthic fauna attest to conditions of exacerbated oxygen deficiency interpreted to represent enhanced water column stratification and

Figure 5-12 Simplified depositional model proposed for each of the different lithology present at El Pujal. The size of the arrows represent the relative magnitude of each variable.

augmented influx of export production. Furthermore, lower TAR values permit to postulate heightened *in-situ* primary production to the point of diluting the TAR signal.

5.6 Conclusions

The results of a high-resolution lithostratigraphic and geochemical study of the basal 13.77 m El Pujal section in the semi-restricted Organyà Basin, south-central Spanish Pyrenees allow to conclude as follows:

1. - The $\delta^{13}\text{C}_{\text{org}}$ signal reveals a temporal pattern similar to those recorded for carbon isotope segment C5 in the pelagic sections of the Swiss Préalpes (Roter Sattel), southern Italian Alps (Cismon) and the hemipelagic section of the south-central Spanish Pyrenees (El Pui). Additional corroborating evidence from the biostratigraphic framework documents the presence of *L. cabri* thus situating the section within this biozone well-recognized within OAE1a. This implies that the El Pujal section is in continuity with the nearby El Pui section and more precisely further extends carbon isotope segment C5.
2. - Integration of sedimentological, micropaleontological, and geochemical data provides a sequence of events that reveal intermittent changes in fluxes of land-derived biolimiting nutrients concurrent with variations in major elements, TOC, RSTEs and benthic fauna. These fluctuations are reflective of water column oxygen level regulated by regional hydrologic fluctuations and riverine supplies that affected OM production and preservation. Similar fluctuating coeval sedimentary facies recorded in other Tethyan sections and partially reproducible worldwide for the period associated with OAE1a reveal possible indeterminate climate variability recorded in the continuous succession of the Organyà Basin.
3. - Variations in redox proxies throughout the studied section imply continuous OM accumulation under impoverished oxygen conditions punctuated by episodes of dysoxia without an anoxic phase which is the hallmark of OAE1a at most sites elsewhere.

The results underscore how unique conditions associated with semi-restricted basins and type of adjacent geologic terranes can play a critical role in modulating divergent sedimentation and carbon sequestration under global forcing factors.

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5.9 Appendices

Appendix 5A Carbon geochemistry values for the 13.77 m section with their respective sample ID and stratigraphic position.

Sample ID	Height (m)	$\delta^{13}\text{C}$	TIC (CaCO_3 %)	TOC (C wt%)
C-15-42	13.77	-24.23	76.07	0.91
C-15-41	13.36	-24.17	72.95	1.12
C-15-40	12.96	-24.12	74.22	0.97
C-15-39	12.54	-24.09	66.54	1.25
C-15-38	12.2	-24.09	65.33	1.34
C-15-37	11.95	-24.20	65.00	1.27
C-15-36	11.67	-24.14	67.33	1.18
C-15-35	11.3	-23.93	69.58	1.17
C-15-34	10.9	-23.96	70.26	1.25
C-15-33	10.55	-23.81	70.77	1.23
C-15-32	10.2	-23.87	73.75	0.96
C-15-31	9.78	-23.86	67.38	1.28
C-15-30	9.48	-23.97	75.88	0.80
C-15-29	9.1	-23.75	71.77	1.05
C-15-28	8.7	-23.81	71.04	1.18
C-15-27	8.33	-23.75	70.72	1.17
C-15-26	7.98	-23.76	72.24	1.12
C-15-25	7.67	-23.73	67.13	1.26
C-15-24	7.4	-24.03	73.82	1.03
C-15-23	7.12	-23.80	73.22	0.99
C-15-22	6.82	-23.91	72.09	1.09
C-15-21	6.45	-23.71	68.47	1.19
C-15-20	6.09	-23.85	66.17	1.15
C-15-19	5.82	-23.75	62.03	1.68
C-15-18	5.52	-24.18	63.66	1.73
C-15-17	5.15	-23.82	67.79	1.39
C-15-16	4.74	-23.80	70.35	1.43
C-15-15	4.38	-23.39	74.53	1.28
C-15-14	4.03	-23.55	76.82	1.19
C-15-13	3.68	-23.49	72.12	1.49
C-15-12	3.32	-23.13	77.61	1.15
C-15-11	3.04	-23.15	78.09	1.25
C-15-10	2.79	-23.18	77.30	1.21
C-15-9	2.52	-23.05	77.28	0.99
C-15-8	2.2	-23.34	76.20	1.14
C-15-7	1.84	-22.84	74.09	1.19
C-15-6	1.47	-22.85	72.15	1.42
C-15-5	1.12	-23.20	79.84	0.95
C-15-4	0.82	-22.58	79.48	1.09
C-15-3	0.55	-22.55	78.30	0.99
C-15-2	0.25	-22.63	78.75	0.80
C-15-1	0	-22.59	76.60	1.18

Appendix 5B Absolute values of terrestrially derived elements (Al, Si, Ti), biolimiting elements (Fe, P), RSTEs (V, Ni, Co, Cr, Cu, Mo) and redox index (Th/U). Concentrations ppm = parts per million.

Sample ID	Height (m)	Al	Si	Ti	Fe	P	V	Ni	Co	Cr	Cu	Mo	Th/U
C-15-42	13.77	17761	51579	641	7787	150	26.0	29.3	1.1	32.3	4.9	1.2	2.0
C-15-41	13.36	19509	55742	711	8673	160	27.6	34.6	0.6	35.5	5.3	1.8	2.2
C-15-40	12.96	18385	52829	666	8149	153	26.0	43.9	0.6	36.8	5.5	2.3	2.0
C-15-39	12.54	23037	67392	872	10811	264	36.4	33.1	0.6	38.7	6.2	1.8	2.8
C-15-38	12.2	27125	77468	957	11573	238	41.0	34.2	0.9	43.9	7.1	1.7	3.0
C-15-37	11.95	27698	75073	974	10702	226	39.1	40.4	0.6	42.8	7.2	1.9	3.0
C-15-36	11.67	23730	66954	866	10427	216	36.6	41.0	0.4	41.4	7.0	2.1	3.5
C-15-35	11.3	22009	60247	775	10867	195	32.3	24.0	0.4	32.7	5.7	1.2	1.9
C-15-34	10.9	21565	59415	840	8710	188	30.8	33.5	0.4	35.4	5.2	1.7	2.8
C-15-33	10.55	20962	58267	824	9866	214	29.8	43.8	0.8	37.6	5.5	2.4	2.5
C-15-32	10.2	18229	52329	704	8282	195	26.6	32.1	0.7	34.5	4.5	1.4	2.6
C-15-31	9.78	23541	70231	919	11327	264	35.2	45.2	1.2	46.7	6.1	2.5	3.2
C-15-30	9.48	18122	49975	681	7798	239	27.5	28.6	0.6	32.8	4.6	1.1	2.5
C-15-29	9.1	18810	54860	712	8871	177	30.9	37.3	0.8	36.4	5.4	2.0	1.7
C-15-28	8.7	20196	56015	752	8806	174	32.3	30.3	0.6	41.1	5.1	1.4	2.6
C-15-27	8.33	20712	58128	796	9614	189	32.0	30.9	0.5	34.8	5.3	1.5	2.6
C-15-26	7.98	20307	56625	722	8776	214	30.7	27.3	0.9	34.1	4.9	1.3	2.7
C-15-25	7.67	26030	68933	942	10456	254	39.6	40.7	1.3	46.3	6.1	2.0	3.6
C-15-24	7.4	20022	53403	691	8320	171	32.3	33.1	1.6	36.4	5.0	1.5	2.7
C-15-23	7.12	19390	53176	757	8936	188	33.3	29.9	2.1	37.1	5.6	1.5	2.0
C-15-22	6.82	21156	57519	772	8833	188	32.9	32.5	0.9	39.9	5.0	1.5	2.5
C-15-21	6.45	34762	89223	1143	14194	283	49.3	48.3	1.5	58.5	7.7	2.6	3.0
C-15-20	6.09	34710	97770	1304	15255	361	57.8	64.9	1.3	68.0	9.3	3.5	3.0
C-15-19	5.82	40502	106870	1388	15919	396	60.5	88.0	2.5	82.0	10.4	3.6	3.6
C-15-18	5.52	37687	97865	1267	15425	357	56.1	96.1	2.9	89.6	10.7	5.0	3.0
C-15-17	5.15	31605	87444	1102	14119	302	48.4	57.6	2.1	62.2	8.2	3.8	2.5
C-15-16	4.74	19167	50785	707	9357	185	30.5	55.9	1.4	45.2	5.7	3.5	2.5
C-15-15	4.38	22162	62226	831	11606	200	35.1	45.5	0.7	46.4	6.3	2.5	1.7
C-15-14	4.03	18382	54459	705	10395	236	30.5	51.4	0.7	44.3	6.4	3.0	2.0
C-15-13	3.68	23721	64569	822	11771	275	42.0	44.8	1.6	49.5	7.9	2.4	2.2
C-15-12	3.32	18232	50397	690	9774	263	31.9	56.8	0.6	43.0	6.2	3.3	2.3
C-15-11	3.04	18717	50274	630	9052	243	30.6	51.5	1.1	42.3	6.1	2.8	1.8
C-15-10	2.79	19379	49210	658	8815	215	31.2	50.1	0.7	42.5	6.2	2.6	2.2
C-15-9	2.52	14626	40878	549	6530	199	23.6	33.6	1.1	30.8	4.6	1.6	2.0
C-15-8	2.2	21503	57957	774	9697	217	34.0	38.1	1.2	56.5	6.4	1.8	2.3
C-15-7	1.84	24086	65027	867	11040	262	36.9	48.4	1.0	49.1	6.8	2.8	2.5
C-15-6	1.47	26022	70920	939	11079	230	40.1	56.6	0.9	51.3	7.9	3.1	2.2
C-15-5	1.12	17252	46366	668	9276	268	28.1	39.4	0.5	34.7	5.1	2.1	2.5
C-15-4	0.82	17325	43487	649	9019	298	24.7	50.5	0.9	38.4	6.2	3.0	1.6
C-15-3	0.55	20125	54038	727	9403	229	27.5	51.6	1.1	45.0	6.3	2.9	2.6
C-15-2	0.25	20312	55129	778	9881	290	28.8	46.8	1.8	46.7	7.0	1.9	2.7
C-15-1	0	22201	60407	817	10664	280	29.8	54.0	1.9	59.4	7.1	2.3	3.0
Average %RSD		9.6	4.7	2.9	3.5	14	1.1	4.7	11	5.7	5.8	6.1	

Appendix 5C Values of various n-alkane and acyclic isoprenoid based parameters.

Sample ID	Height (m)	TAR	Pr/Ph	Pr/n C ₁₇	Ph/n C ₁₈	n C ₁₇ /n C ₃₁	ACL
C-15-42	13.77	0.3	1.6	0.3	0.2	5.3	27.0
C-15-41	13.36	0.3	1.7	0.2	0.2	5.4	27.0
C-15-40	12.96	0.4	1.2	0.3	0.2	4.9	27.2
C-15-39	12.54	0.3	1.8	0.3	0.2	7.7	26.9
C-15-38	12.2	0.2	1.2	0.2	0.2	7.2	27.1
C-15-37	11.95	0.2	1.5	0.3	0.2	8.9	26.9
C-15-36	11.67	0.3	1.6	0.3	0.2	5.8	27.0
C-15-35	11.3	0.3	1.7	0.3	0.2	5.3	27.0
C-15-34	10.9	0.3	1.4	0.3	0.2	5.4	27.0
C-15-33	10.55	0.3	1.9	0.3	0.2	8.3	26.8
C-15-32	10.2	0.2	2.3	0.3	0.2	7.8	27.0
C-15-31	9.78	0.2	1.7	0.4	0.2	7.3	26.9
C-15-30	9.48	0.2	1.8	0.3	0.1	11.6	26.9
C-15-29	9.1	0.3	1.5	0.3	0.2	5.4	27.3
C-15-28	8.7	0.3	1.4	0.3	0.2	6.4	27.2
C-15-27	8.33	0.3	1.3	0.2	0.2	5.6	27.2
C-15-26	7.98	0.2	1.8	0.3	0.2	6.7	27.1
C-15-25	7.67	0.2	2.0	0.3	0.2	18.8	26.7
C-15-24	7.4	0.2	1.6	0.3	0.2	8.6	26.8
C-15-23	7.12	0.2	2.0	0.4	0.2	7.0	27.0
C-15-22	6.82	0.1	2.1	0.4	0.2	18.0	26.6
C-15-21	6.45	0.1	1.9	0.4	0.2	20.9	26.5
C-15-20	6.09	0.1	1.3	0.4	0.3	37.1	26.5
C-15-19	5.82	0.1	2.0	0.4	0.2	22.0	26.6
C-15-18	5.52	0.1	1.3	0.4	0.3	60.6	26.0
C-15-17	5.15	0.1	2.2	0.4	0.2	24.3	26.6
C-15-16	4.74	0.1	1.8	0.4	0.3	25.3	26.5
C-15-15	4.38	0.1	1.8	0.4	0.2	24.3	26.5
C-15-14	4.03	0.4	2.1	0.3	0.2	5.0	27.0
C-15-13	3.68	0.1	2.1	0.5	0.3	18.8	26.7
C-15-12	3.32	0.3	1.5	0.3	0.2	4.7	27.2
C-15-11	3.04	0.3	1.6	0.4	0.2	5.3	27.1
C-15-10	2.79	0.3	1.6	0.3	0.2	5.3	27.1
C-15-9	2.52	0.3	1.9	0.3	0.2	5.1	27.1
C-15-8	2.2	0.3	2.3	0.4	0.2	9.6	26.9
C-15-7	1.84	0.2	2.2	0.3	0.2	8.0	27.0
C-15-6	1.47	0.2	2.1	0.4	0.2	12.0	26.8
C-15-5	1.12	0.3	2.3	0.5	0.2	7.4	27.0
C-15-4	0.82	0.2	1.9	0.4	0.2	11.9	26.7
C-15-3	0.55	0.2	2.0	0.5	0.2	10.7	26.8
C-15-2	0.25	0.2	2.0	0.5	0.2	8.0	26.8
C-15-1	0	0.2	2.7	0.5	0.2	8.5	26.8

Appendix 5D Summary of scores and loadings from the PCA.

Scores			Loadings		
Stratigraphic Height (m)	PC1	PC2	Variable	PC1	PC2
0	1.0252	1.1335	TIC	-0.208	0.4605
0.25	-0.623	1.1444	TOC	0.2243	0.0168
0.55	-0.879	1.6063	Si	0.2788	-0.184
0.82	-1.911	3.2195	Al	0.2836	-0.129
1.12	-2.87	1.0964	Ti	0.2807	-0.158
1.47	1.7181	1.107	Fe	0.2811	-0.007
1.84	0.3457	1.0413	P	0.2359	0.1854
2.2	-0.902	0.9989	V	0.2798	-0.097
2.52	-4.438	0.8162	Cr	0.2757	0.1777
2.79	-1.867	1.3081	Co	0.2042	0.221
3.04	-1.707	2.0341	Ni	0.2377	0.3491
3.32	-1.524	1.7523	Cu	0.2765	0.1245
3.68	1.8746	0.9135	Mo	0.2128	0.3949
4.03	-1.597	1.7911	Th/U	0.1702	-0.37
4.38	0.3305	1.1983	Foram ρ	-0.178	0.3548
4.74	0.7263	0.8795	TAR	-0.223	-0.001
5.15	5.5609	0.4106	ACL	-0.224	-0.179
5.52	10.743	1.9524			
5.82	10.311	-0.369			
6.09	7.0863	-0.445			
6.45	4.6571	-0.72			
6.82	-1.286	-0.341			
7.12	-2.006	0.3414			
7.4	-1.871	-0.468			
7.67	1.5785	-1.38			
7.98	-2.205	-1.119			
8.33	-2.164	-1.096			
8.7	-2.087	-1.278			
9.1	-2.298	-0.586			
9.48	-3.037	-0.856			
9.78	1.5406	-1.487			
10.2	-2.763	-0.907			
10.55	-0.84	-0.303			
10.9	-1.589	-1.683			
11.3	-1.764	-1.598			
11.67	0.5801	-2.312			
11.95	1.5893	-2.331			
12.2	1.7653	-2.667			
12.54	0.1669	-1.979			
12.96	-3.104	0.0583			
13.36	-2.601	-0.509			
13.77	-3.669	-0.37			

6 REGIONAL PALEOENVIRONMENTAL INFLUENCE ON OM SEQUESTRATION AND CHARACTERISTICS OF CARBON ISOTOPE SEGMENT C5 IN A HEMIPELAGIC SEQUENCE, ORGANYÀ BASIN, NORTHEAST SPAIN

Socorro, J., Maurrasse, F.J-M.R., 2020. Regional paleoenvironmental influence on OM sequestration and characteristics of carbon isotope segment C5 in a hemipelagic sequence, Organyà Basin, northeast Spain. The Depositional Record. Accepted – In Revision.

Abstract

The Cretaceous marine sedimentary record is punctuated by brief episodes of unusually high rates of organic carbon burial termed Oceanic Anoxic Events (OAEs). The El Pujal Section consists of an expanded series of limestones, argillaceous limestones and marlstones that chronicles the response to perturbations of the global carbon cycle associated with OAE1a in a hemipelagic setting of the Organyà Basin. In this study, we aim to understand the lithological and geochemical responses to changing paleoenvironmental conditions associated with carbon isotope segment C5 of OAE1a. We apply a multi-proxy approach to characterize how regional factors influenced the accumulation of organic-rich sediments during this period of severe oxygen deficient conditions in the ocean.

Results from biomarker thermal maturity indices suggest that the sediments are thermally immature; therefore, the preserved organic geochemical data characterizes the original signal. Source specific biomarkers demonstrate that the bulk organic matter (OM) derives from *in-situ* production, with lesser inputs from allochthonous sources. High-resolution stable carbon isotope data ($\delta^{13}\text{C}_{\text{org}}$) permits to establish refined details of segment C5 within OAE1a not perceivable in correlative sections elsewhere. Pulses of fluvial fluxes associated with climatic fluctuations supplied variable quantities of

terrestrially derived OM with more negative isotopic values, which left their intrinsic signature superimposed on the global $\delta^{13}\text{C}_{\text{org}}$ signal of segment C5 as minor negative spikes. Pulses of fluvial discharge also explain the alternating lithology with limestones representing the least terrestrially influenced end-member and marlstones representing episodes of highest terrigenous influence.

Primary production sustained by fluvial inputs of biolimiting elements provided abundant labile OM conducive to oxygen-deprived conditions as attested by concomitant peaks in TOC, relatively lower benthic faunal counts, lower bioturbation index, higher concentration of pyrite and enrichments in RSTEs. The presence of gammacerane in marlstone intervals implies a stratified water column, which may have been a controlling factor in preventing vertical mixing and oxygenation of the basin. However, OM preservation was not chiefly controlled by redox condition as physical encapsulation by clay minerals likely played a significant role. In addition, coincident inputs of terrestrial OM with more recalcitrant properties and prone to be bound to clay minerals resulting from soil forming processes supplemented the accumulation of OM, especially during intervals of enhanced terrigenous fluxes. Appraisal of the aromatic lipid fraction revealed elevated concentrations of perylene coeval with increases in biomarkers indicative of allochthonous OM, thus supporting its link with terrestrial vegetation input. Perylene occurrence at El Pujal covaries closely with intervals of more humid climatic conditions. Given its demonstrated link with wood degrading fungi, high abundance of sedimentary perylene might therefore serve as a biomarker indicating a moist continental climate in the depositional setting.

This study further highlights the continuous local expression of OAE1a in the hemipelagic setting of the semi-restricted Organyà Basin. The combined result underscore how despite sharing common global forcing factors, regional paleoenvironmental conditions are probably more important in determining the sedimentary expression of OAE1a.

6.1 Introduction

The Cretaceous marine sedimentary record is punctuated by brief episodes of severe oxygen depletion in bottom waters termed Oceanic Anoxic Events (OAEs) (Schlanger and Jenkyns, 1976; Jenkyns, 1980; Leckie et al., 2002). These short-lived episodes lasting ~ 1 Myr (Li et al., 2008) are characterized by sediments with unusually high content of organic carbon and distinct positive shifts in the stable carbon isotope ($\delta^{13}\text{C}$) record of marine sediments on a global scale (e.g. Scholte and Arthur, 1980; Erbacher et al., 1996; Hasegawa, 1997; Menegatti et al., 1998; Leckie et al., 2002; Herrle et al., 2004). The Early Aptian OAE1a, also known as the Livello Selli or Goguel event, represents one such event with its global signal recorded in organic matter (OM)-rich marine sediments of various settings (Schlanger and Jenkyns, 1976; Arthur and Schlanger, 1979; Coccioni et al., 1987; Menegatti et al., 1998; Arthur et al., 1990; Bellanca et al., 2002; Dumitrescu and Brassell, 2005; 2006; Luciani et al., 2006; Ando et al., 2008; Heldt et al., 2008; Roban and Melinte-Dobrinescu, 2012; Aguado et al., 2014a,b; Sanchez-Hernandez and Maurrasse, 2014; 2016). In general, these sediments tend to be pyritic, laminated, enriched in redox sensitive trace elements (RSTEs), lack diversity, or may be devoid of benthic organisms.

The geochemical hallmark of OAE1a is a distinct $\delta^{13}\text{C}$ signature which begins with a pronounced negative shift, recognized as segment C3 (Menegatti et al., 1998) succeeded by more positive values during segments C4 through C6 (Menegatti et al., 1998). The negative carbon isotope excursion (CIE) reported for segment C3 has been interpreted as ensuing from massive outgassing of large quantities of isotopically light CO_2 ($\delta^{13}\text{C} \sim -5\text{‰}$), related to the emplacement of the Ontong Java-Manihiki-Hikurangi large igneous province (LIP) (e.g. Larson, 1991; Tarduno et al., 1991; Ingram et al., 1994; Larson and Erba, 1999; Méhay et al., 2009; Tejada et al., 2009). The C3 negative CIE has also been attributed to rapid dissociation of methane hydrates ($\delta^{13}\text{C} \sim -60\text{‰}$) (Kvenvolden, 1993) into the atmosphere (e.g. Jahren et al., 2001; 2005; Beerling et al., 2002; van Breugel et al., 2007). The subsequent positive trend ($\delta^{13}\text{C}$ excursion segments C4 – C6) is accepted to represent periods of enhanced OM sequestration because primary productivity in the ocean preferentially takes up the lighter carbon (^{12}C), thus leaving the remaining global carbon reservoir enriched in ^{13}C (Arthur et al., 1988; Weissert, 1989; Arthur et al., 1990; Menegatti et al., 1998; Leckie et al., 2002; Jenkyns, 2010; van Bentum et al., 2012). The effects of these perturbations on the global carbon reservoir are expressed on the synchronicity of the isotopic shifts which manifests in marine carbonates ($\delta^{13}\text{C}_{\text{carb}}$) (Menegatti et al., 1998; Moullade et al., 1998; Kuhnt et al., 1998; Erba et al., 1999; Bellanca et al., 2002; de Gea et al., 2003; Herrle et al., 2004; Heldt et al., 2008; Michalík et al., 2008; Moreno-Bedmar et al., 2009; Masse and Fenerci-Masse, 2011; Elkhazri et al., 2013; Papp et al., 2013; Godet et al., 2014; Graziano and Raspini, 2018) and OM ($\delta^{13}\text{C}_{\text{org}}$) from both marine (Menegatti et al., 1998; Dumitrescu and Brassell, 2006; Millán et al., 2009; Gaona-Narvaez et al., 2013a; Sanchez-Hernandez et al., 2014; Sanchez-

Hernandez and Maurrasse, 2016) and terrestrial sources (Gröcke et al., 1999; Ando et al., 2002). Thus, the consistency and reproducibility of the carbon isotope shifts in widely distributed locations during OAE1a provide a robust chronostratigraphic tool for stratigraphic correlation (e.g. Scholle and Arthur, 1980; Weissert and Bréhéret, 1991; Menegatti et al., 1998; Herrle et al., 2004). Nonetheless, noticeable lithologic and isotopic variations develop regionally and locally as specific responses related to basin physiography, atmospheric and basinal circulation patterns, water chemistry, ecosystem structure and dynamics, as well as the amount and type of terrestrial fluxes (Jenkyns, 1995; Moullade et al., 1998; Grötsch et al., 1998; Danelian et al., 2004; Yilmaz et al., 2004; Immenhauser et al., 2005; Dumitrescu and Brassell, 2006; Chaabani and Razgallah, 2006; Heldt et al., 2010; Huck et al., 2010; Najarro et al., 2011; Stein et al., 2012; Gaona-Narvaez et al., 2013a, 2013b; Sanchez-Hernandez et al., 2014; Núñez-Useche et al., 2015; Sanchez-Hernandez and Maurrasse, 2016).

The Organyà Basin located in the Iberian Peninsula (Fig. 6-1A, B) developed as a semi-enclosed basin during the Early Cretaceous, and previous studies document extensive successions of continuous hemipelagic marls and limestones (Peybernès and Souquet, 1973; Berástegui et al., 1990; Bachmann and Willems, 1996; García-Senz, 2002; Bernaus et al., 2000, 2002, 2003; Gong et al., 2009; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Llaguno, 2017; Socorro and Maurrasse, 2019). This study further extends our analyses of the Early Aptian related to OAE1a at the El Pujal section (Fig. 6-1C, D) (Socorro and Maurrasse, 2019) and aims at understanding the lithological and geochemical responses to changing paleoenvironmental conditions associated with carbon isotope segment C5. We apply a multi-proxy

Figure 6-1 A) Location map of the Organyà Basin in the Iberian Peninsula. B) Regional geologic map showing the area of interest. A) and B) modified from Dinarès-Turell and García-Senz, 2000). C) Detailed geologic map of the studied area showing the location of the El Pui Section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) and the El Pujal Section (Socorro and Maurrasse, 2019; and this study). C) Modified from Gong et al. (2009). D) Satellite image showing the portion of the El Pujal Section studied thus far. Basal portion refers to a previous study by Socorro and Maurrasse (2019). D) Modified from Google Earth Map Data 2018. E) Photograph of the outcrop showing the expanded sequence of hemipelagic sediments exposed as differentially weathered packets.

methodology to better characterize the local factors that resulted in the accumulation of organic-rich sediments during this period known for widespread severe oxygen deficient

conditions. The results provide additional insight on the effects of regional factors during intervals of enhanced OM sequestration, and how the input of terrestrial vegetation linked with lower values of $\delta^{13}\text{C}_{\text{org}}$ may have altered the global $\delta^{13}\text{C}_{\text{org}}$ archive in the Organyà Basin. The expanded section generated a $\delta^{13}\text{C}_{\text{org}}$ curve with great detail of an amplified record suitable for more precise chemostratigraphic correlations.

6.2 Geologic Framework

From the Late Jurassic to the Early Cretaceous the gradual opening of the North Atlantic Ocean led to the separation of the Iberian Plate from Eurasia and Africa (Srivastava et al., 1990; Olivet, 1996; Vergés et al., 2002; Sibuet et al., 2004). The Bay of Biscay opened concurrently with this rifting phase while Iberia underwent $\sim 35^\circ$ counter-clockwise rotation relative to Eurasia (Van der Voo, 1969; Williams, 1975; Montadert et al., 1979; Montigny et al., 1986; Srivastava et al., 1990; Sibuet and Collette., 1991; Choukroune, 1992; Rosenbaum et al., 2002; Sibuet et al., 2004; Gong et al., 2008; Vissers and Meijer., 2012). The syn-rotational rifting along the northern portion of the Iberian plate produced significant extensional faulting which generated a series of pull-apart depocenters, including the Central Pyrenean Basin that is associated with the Organyà deposits (Fig. 6-1B). The basin became inverted due to the onset of convergence between Africa, Iberia and Europe in the Late Cretaceous (Puigdefàbregas and Souquet, 1986; Berástegui et al., 1990; Vergés and Muñoz, 1990; Muñoz, 1992; Vergés and García-Senz., 2001; García-Senz, 2002; Golonka, 2004). The paleogeographic position of the Organyà Basin in the Early Cretaceous was on the northern margin of the Ebro block with an estimated width of at least 15 km and between 70 km to 100 km long along its extensional axis (Dinarès-Turell and García-Senz, 2000; Vacherat et al., 2017). It accommodated a continuous

4,000 m sequence of shallow platform carbonates, and hemipelagic to pelagic marine sediments from the upper Tithonian to the lower Turonian, after which the basin fill was inverted and thrust southward along a detachment fault in a compressional phase associated with the Pyrenean orogeny (Berástegui et al., 1990; Vergés and García-Senz., 2001; García-Senz, 2002). Sedimentary deposits of the Organyà Basin situated in the South Pyrenean Central Unit (SPCU) comprise a complex series of thrust sheets (e.g. Bóixols and Montsec; Cotiella and Pedraforca nappes; and the Sierras Marginales (Seguret, 1972; Vergés and Muñoz, 1990; Puigdefàbregas et al., 1992; García-Senz, 2002). Remnants of the Basin outcrop in the hanging wall of the Bóixols thrust system, bounded to the north by the Morreres backthrust (Fig. 6-1C) (García-Senz, 2002; Gong et al., 2009). A prominent E-W trending asymmetric syncline (Santa Fé syncline) divides the northern, relatively thick limb, from a thinner southern limb (Gong et al., 2009). Structurally the outcrop is located along the northern limb of the Santa Fé syncline (42°13'06.15"N, 1°18'55.85"E), and on the south side of the Cabó River valley in the municipality of Organyà (Fig. 6-1C). Previous studies of lower beds exposed on the north side of the valley reported the record of OAE1a up to carbon isotope segment C5 (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016), which has been correlated with the lowermost part of the El Pujal section (Socorro and Maurrasse, 2019).

Here, we investigate 70.75 m of the succession in continuity with the previously discussed 13.77 m basal segment of the El Pujal Section (Fig. 6-1D) (Socorro and Maurrasse, 2019), which consists of a succession of limestones, argillaceous limestones and marlstones exposed as differentially weathered packets (Fig. 6-1E).

6.3 Materials and Methods

6.3.1 Field Sampling and Microscopy

Field sampling of the present study extends from 14.29 m to 85.04 m (70.75 m) with a total of 109 samples collected at an average resolution of 1 sample per 65 cm. Samples were selected based on apparent bedding and the top ~ 1 m surface of the weakly lithified layers was cleared away to ensure collection of unweathered rocks. Color description of samples is based on the modified Munsell color system as proposed by Goddard et al., (1963).

A total of 109 thin sections were analyzed using an Olympus BH-2 light transmitting microscope. The microscopic analysis focused on microfacies, mineralogical composition, index fauna identification, bioturbation, presence/absence of benthic fauna, and minerals indicative of redox conditions. The micropaleontological analysis of planktonic foraminifera was accomplished primarily using the help of illustrations in the published literature (e.g. Verga and Premoli-Silva, 2002; Heldt et al., 2008; Moullade et al., 2015). Visual estimates of allochems follow Shvetsov's proposed percentage diagrams as summarized by Terry and Chilingarian, (1955). A bioturbation index was assigned to each sample following the proposed scheme in Taylor and Goldring (1993). In addition, a sample count of benthic fauna focused on benthic foraminifera and echinoid fragments. The total counts were divided by the area of each thin section and are expressed as density (ρ) or number of specimens per cm^2 .

6.3.2 Carbon Analyses

All samples ($n = 109$) were analyzed for total carbon (TC) and total inorganic carbon (TIC) at Florida International University (FIU) using a LECO CR-412 carbon

analyzer following the methodology used in our Carbon Analysis Laboratory (Ponton, 2005; Gaona-Narvaez et al., 2013b; Sanchez-Hernandez and Maurrasse, 2014), and modified as proposed by Socorro and Maurrasse (2019). The LECO CR-412 instrument uses an infrared cell to measure the total CO₂ produced by the combustion at 1450 ± 2°C of 0.3000 g of a powdered rock sample (Gaona-Narvaez et al., 2013b; Sanchez-Hernandez and Maurrasse, 2014). Calibration of the instrument was performed by producing a 15-point, best-fit calibration curve (0.0500 g, 0.0700 g, 0.1000 g, 0.1200 g, 0.1500 g, 0.1700 g, 0.2000 g, 0.2200 g, 0.2500 g, 0.2700 g, 0.3000 g, 0.3200 g, 0.3500 g, 0.3700 g, 0.4000 g) using pure calcite ≥ 99.0% (C64-500, Fisher Scientific) (Sanchez-Hernandez and Maurrasse, 2014). Analytical precision was estimated at 0.03% or better, based on 4 replicate analyses of the same sample and accuracy was verified by analyzing a reference material (Dolomitic Limestone NIST 88b). TIC values are reported as CaCO₃ % and are used to assign a general lithologic nomenclature modified from Sanchez-Hernandez and Maurrasse (2014) to allow for a wider range of representation of lithologic variation observed in the field. Hence, TIC > 70% = limestone, 65-70% = argillaceous limestone and 35-65% = marlstone. Total organic carbon (TOC) was determined by taking the difference between TC and TIC (TC-TIC) and dividing the result by 8.33, thus TOC is expressed as C wt% (detailed in Sanchez-Hernandez and Maurrasse, 2014).

For stable carbon isotope analysis on the organic fraction ($\delta^{13}\text{C}_{\text{org}}$) powdering and de-carbonation of samples (n = 109) follow the procedures outlined in Socorro and Maurrasse (2019). Analysis of the samples were conducted at the Rosenstiel School of Marine and Atmospheric Science (RSMAS) stable isotope laboratory (SIL) using a

Costech elemental combustion system interfaced with a Thermo Scientific Delta V Advantage continuous flow isotope ratio mass spectrometer. $\delta^{13}\text{C}_{\text{org}}$ results are reported in per mil (‰) relative to the Vienna Pee Dee Belemnite standard (VPDB).

6.3.3 Major and Redox Sensitive Trace Elements (RSTEs) Analysis

Samples ($n = 65$) were analyzed for major (Si, Al, Ti, P, Fe) and RSTEs (V, Cr, Co, Ni, Cu, Mo, U) at the FIU Trace Evidence Analysis Facility (TEAF) using an ELAN DRC II (Perkin Elmer LAS) inductively coupled plasma mass spectrometer (ICP/MS). Sample introduction was achieved through laser ablation (LA) using a 266 nm Nd-YAG laser (LSX 500, CETAC) set at a spot size of 200 μm and 10 Hz. Sample preparation and calibration followed the methodology developed by Arroyo et al., (2009) and outlined in Sanchez-Hernandez and Maurrasse (2014), and Socorro and Maurrasse (2019). Results for major elements are expressed as parts per thousand ($\text{ppm} \cdot 10^{-3}$) and RSTEs are expressed as parts per million (ppm).

Additionally, because RSTEs show significant enrichments under reducing conditions relative to the average background value (Wedepohl, 1971, Tribovillard et al., 2004), enrichment indices (EIs) were calculated based on the average values of the section (e.g. Bodin et al., 2007; Socorro and Maurrasse, 2019). Usually, the background level for these elements is taken from those reported for average shale values such as the Post Archean Australian Shale (PAAS) of Taylor and McLennan (1985), the North American Shale Composite (NASC) of Gromet et al, (1984) or the average shale value (ASV) of Turekian and Wedepohl (1961), Wedepohl (1971, 1991). As discussed in Socorro and Maurrasse (2019) this method may overlook the critical effects of crustal heterogeneity, chemical fractionation during weathering, and grain-size sorting that can

produce sediments very specific to the region of interest (Van der Weijden, 2002; Brumsack, 2006; White, 2013). Thus, depending on the area, the detrital portion of the sediment may have a chemical composition that substantially differs from those reported for the “average shale”. For example, given an element with a relatively low crustal abundance, but the parent rock of the sediments in the adjacent region are enriched in such element, the EIs calculated for this element will be artificially inflated, even though the value might be even lower than the regional’s background average value. Therefore, an assessment of the regional lithological background value (Cole et al., 2017) is required before calculating EIs. Based on uncertainties about the magnitude of the background natural value of the regional detrital signal unrelated to the redox conditions at time of deposition, here we rely on a baseline of the Organyà Basin’s Average Background Value (OBABV) unique to the region, modified from the earlier study (Socorro and Maurrasse., 2019). Hence, the EI values should be more representative of the true detrital signal of the Organyà Basin watershed. Extensive studies for the period spanning the latest Barremian to the early Aptian provided reliable data to calculate the OBABV by combining RSTEs values from 4 studied upper Barremian – lower Aptian hemipelagic to pelagic sections at various sites of the basin. These include: 1) the El Pui section (233.3 m) with a total of 84 samples (Sanchez-Hernandez, 2014); 2) the Eastern Prada Quarry Section (27.98 m) with 31 samples (Llaguno, 2017); 3) the Cabó Section (35.6 m) with 17 samples (Carlos Herdocia - Appendix 6A); and 6D) the basal portion of the El Pujal Section (13.77 m) with 42 samples (Socorro and Maurrasse, 2019). The OBABV presented here also includes new data obtained for this study (70.75 m) with 65 samples (Table 6-1).

Table 6-1 Calculated OBABV values for various redox-sensitive elements.

Redox-Sensitive Elements	V	Cr	Co	Ni	Cu	Mo	U
	27.56	33.46	3.68	32.31	5.72	2.56	1.1

The EI for each RSTE relative to the OBABV is calculated using the following equation:

$$EIs = \frac{[RSTEs]}{[RSTEs]_{\text{regional background}}}$$

Here, the numerator [RSTEs] represents the concentration of each sample in ppm, and the denominator [RSTEs]_{regional background} is the average value in ppm of the corresponding RSTE from the OBABV as discussed above. Relative enrichments are thus expressed as EIs > 1, whereas depleted elements are represented by EIs < 1. To allow for easier correlation between RSTEs and other proxies, we calculated the sum of all enrichment indices $\sum EIs$ by adding all the EIs of each element for each sample.

6.3.4 Clay Mineral Analysis (< 2 μm Fraction)

Based on the lithological characteristics of the section provided by the TIC and TOC, seven samples (n = 7) were selected for X-ray diffraction (XRD) analysis to represent the different temporal variations of terrigenous supply to the basin. The analyses were performed at the Illinois State Geological Survey (ISGS), Geochemistry Section, Prairie Research Institute, University of Illinois. The methodology used is as follows: 1) each sample was gently ground, sieved and the < 250- μm fraction was collected; 2) 15 g of the sample was dispersed in 100 ml deionized (DI) water for 24 hrs; 3) transfer of the sample to a mixer stirring for one minute, and the suspension was then poured back to the beaker and allowed to settle overnight; 4) the next day, 1/3 of the clear supernatant was decanted and the beaker refilled with fresh DI water; 5) two drops of

dispersant (sodium hexa-metaphosphate) were added to the suspension, stirred for one minute and allowed to settle; 6) after 15 min the suspension was transferred onto a glass slide using an eye dropper and dried overnight; 7) all slides were then saturated using ethylene glycol vapors for 48 hrs. The oriented and glycolated clay slides were analyzed with a Scintag® XDS2000 diffractometer. Step-scanned data was collected from 2° to $34^\circ 2\theta$ with a fixed rate of 2° per min with a step size of $0.05^\circ 2\theta$ for each sample. All resulting traces were analyzed using the semi-quantitative data reduction software from Materials Data Inc. (MDI) known as Jade+®.

6.3.5 Lipid Analyses

A total of 64 samples were prepared and extracted following the procedures proposed by Socorro and Maurrasse (2019) and references therein. Briefly, the total lipid extract (TLE) obtained was evaporated until almost dry and dissolved in hexane. Then, the TLE was mounted on a silica gel-packed glass pipette and separated into two fractions (F1 and F2). Fraction F1 containing the aliphatic components was extracted using 4 ml of hexane, and fraction F2 containing the aromatic components was extracted using 4 ml of dichloromethane (DCM).

The aliphatic fractions (F1) ($n = 64$) and the aromatic fractions F2 ($n = 3$) were analyzed using an Agilent 6890/Agilent 5973 gas chromatography mass spectrometer (GC/MS) at the FIU Advanced Mass Spectrometry Facility. The GC was equipped with an HP-5MS UI 30 m, 0.25 mm, 0.25 μm , capillary column. A 5 μL volume of each sample was injected in splitless mode with the injector temperature set at 280°C . The oven temperature program was set to hold at 65°C for 2 min, then ramped to 300°C at a rate of $4^\circ\text{C}/\text{min}$ and held at 300°C for 8 min. Detection was performed by using a single

quadrupole operating in positive mode electron impact ionization (EI⁺) with a scan range from m/z 42 to m/z 500 and a solvent delay time of 4 min.

Selected samples ($n = 5$) were chosen for further purification of hopanes and steranes through the removal of *n*-alkanes. The *n*-alkanes were isolated from the branched and cyclic hydrocarbons using urea adduction. For this, the previously separated aliphatic fraction (F1) was combined in a ratio of 2:1 hexane/acetone (4 ml hexane/2 ml acetone) in a previously cleaned (combusted at 560°C for 2 hrs) 11-dram vial in which 2 ml of a urea saturated methanol (MeOH) solution was added drop-wise. The saturated urea MeOH solution was prepared by dissolving 16.6 g of urea in 100 ml of MeOH at 60°C. The dropwise addition of the urea saturated MeOH solution resulted in the immediate precipitation of white urea crystals. The mixture was allowed to settle overnight and then centrifuged at 2,000 rpm for 5 min to separate the non-adduct fraction from the urea crystals. The non-adduct fraction was collected and stored in a second 11-dram vial. The dry urea crystals were then washed with 3 ml of a 2:1 hexane/acetone solution and the resulting non-adduct solution was combined with the original non-adduct fraction. The urea adduction procedure was repeated 3x on the non-adduct fraction to ensure that all the *n*-alkanes were removed. At the end, the non-adduct fractions containing branched and cyclic hydrocarbons (including hopanes and steranes) were combined and evaporated to ~ 1 ml before GC/MS analysis.

Analysis of the non-adduct fraction ($n = 5$) focused on hopanes and steranes and was conducted at the FIU Advanced Mass Spectrometry Facility. Separation was performed using an Agilent 6890 GC equipped with an UI HP-5MS UI 30 m, 0.250 mm, 0.25 μ m, capillary column. Injections (5 μ L) were performed in splitless mode with an

injector temperature of 280°C. The oven temperature program was set to hold at 65°C for 2 min, then ramped to 300°C at a rate of 4°C/min and hold at 300°C for 8 min. Detection was performed by using a single quadrupole mass spectrometer (Agilent 5973) operating in EI+ mode. The instrument was operated in selective ion monitoring (SIM) with a dwell time of 40 ms and a solvent delay time of 4 min. Identification of analytes was achieved on the basis of comparison of published retention times and mass spectra (Watson et al., 2000; Peters et al., 2005; 2007).

The terrigenous to aquatic ratio (TAR) was determined using the equation proposed by Bourbonniere and Meyers (1996):

$$\text{TAR} = \frac{n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31}}{n\text{C}_{15} + n\text{C}_{17} + n\text{C}_{19}}$$

The relative abundance of odd to even preferences of long-chain length *n*-alkanes were determined using the carbon preference index (CPI) after Bray and Evans (1961):

$$\text{CPI} = \frac{1}{2} \left[\frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{24} + n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32}} + \frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32} + n\text{C}_{34}} \right]$$

The odd to even preferences (OEP) of long-chain length *n*-alkanes was calculated by adapting the OEP equation of Scalan and Smith (1970) to OEP (2) as published in Peters et al. (2007):

$$\text{OEP}(2) = \frac{n\text{C}_{25} + 6 * n\text{C}_{27} + n\text{C}_{29}}{4 * n\text{C}_{26} + 4 * n\text{C}_{28}}$$

Various hopane and sterane parameters were calculated as follows:

$$\frac{T_s}{T_s + T_m} = \frac{18\alpha\ 22,29,30\ \text{trisorneohopane}}{18\alpha\ 22,29,30\ \text{trisorneohopane} + 17\alpha\ 22,29,30\ \text{trisorhopane}}$$

$$C_{31} \frac{22S}{22S + 22R} = \frac{C_{31}\ 17\alpha, 21\beta(H)\ \text{homohopane}\ (22S)}{C_{31}\ 17\alpha, 21\beta(H)\ \text{homohopane}\ (22S) + C_{31}\ 17\alpha, 21\beta(H)\ \text{homohopane}\ (22R)}$$

$$\text{Gammacerane Index} = \frac{C_{30}\ \text{Gammacerane}}{C_{31}\ 17\alpha, 21\beta(H)\ \text{homohopane}\ (22R)}$$

$$\%C_{27}\alpha\alpha\alpha R = \frac{100 * C_{27}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}{C_{27} + C_{28} + C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}$$

$$\%C_{28}\alpha\alpha\alpha R = \frac{100 * C_{28}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}{C_{27} + C_{28} + C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}$$

$$\%C_{29}\alpha\alpha\alpha R = \frac{100 * C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}{C_{27} + C_{28} + C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}$$

$$\frac{C_{27}}{C_{29}} = \frac{C_{27}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}{C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}$$

$$C_{29} \frac{20S}{20S + 20R} = \frac{C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20S)}{C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20S) + C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20R)}$$

$$C_{29} \frac{\beta\beta}{\beta\beta + \alpha\alpha} = \frac{C_{29}\ 5\alpha, 14\beta, 17\beta(H)\ \text{sterane}\ (20S + 20R)}{C_{29}\ 5\alpha, 14\beta, 17\beta(H)\ \text{sterane}\ (20S + 20R) + C_{29}\ 5\alpha, 14\alpha, 17\alpha(H)\ \text{sterane}\ (20S + 20R)}$$

Selected samples (n = 5) were chosen for quantification of polycyclic aromatic hydrocarbons (PAHs). Certified deuterated surrogate PAH mixture (Z-014J-0.5x), p-

Terphenyl-d14 internal standard (M-525-FS-2) and perylene standard solution (H-121S) were purchased from AccuStandard (New Haven, CT, USA). Additional standard mixture EPA 525 PAH Mix A and PAH Mix CRM47543 were purchased from Sigma-Aldrich (St. Louis, Mo, USA). Standard solutions were refrigerated at 4°C until needed. Exactly 5.0000 g (dry weight) of each powdered sample was weighed and transferred to a cleaned (combusted at 560°C for 2 hrs) 11-dram vial. To validate the extraction method and efficiency, 100 µL of the diluted (1 ng/µL) deuterated surrogate PAH mixture (acenaphthene-d10, chrysene-d12, perylene-d12, phenanthrene-d10) was added to each vial prior to solvent extraction. Then, 10 ml of a 1:9 mixture of MeOH to DCM was added to each vial and sonicated for 30 min. Each sample was then centrifuged at 2,000 rpm for 10 min and the sediment-free supernatant transferred to a 4-dram vial. The latter process was repeated with 10 ml 1:9 MeOH/DCM fresh solvent and the extracts combined in the 4-dram vial. Following the extraction, activated copper was added to each extract until the copper turned a black color (~ 3 - 4 hrs), signifying complete reaction with elemental sulfur after which it was removed. The copper was activated by placing it in 10% hydrochloric acid (HCl) solution for approximately 5 min and then washed 3 times with deionized water and three more times with DCM. The total extracts were concentrated by evaporation until almost dry and then solvent-exchanged with 1 ml of hexane. Separation of the aliphatic fraction (F1) from the aromatic fraction (F2) was achieved using a silica gel-packed glass pipette, first eluted with 4 ml of hexane to remove the aliphatic components (F1) and subsequently eluted with 4 ml of DCM (F2). The second fraction (F2) containing the targeted PAHs was evaporated until almost dry and re-dissolved in 100 µL of DCM containing the internal standard, p-Terphenyl-d14 (1

ng/ μ L). In addition, for quality control purposes, 3 additional samples were prepared following the previous procedure: A method blank containing only the deuterated surrogate PAH mixture (1 ng/ μ L), a fortified blank containing the deuterated surrogate PAH mixture (1 ng/ μ L) and the targeted PAH standards (1 ng/ μ L) and a fortified sample containing a powdered sample, the deuterated surrogate PAH mixture (1 ng/ μ L) and the targeted PAH standards (1 ng/ μ L).

The PAH analyses were conducted at the FIU Advanced Mass Spectrometry Facility. Sample injection and GC separation were performed by an Agilent 6890 gas chromatograph equipped with an autosampler and an HP-5MS UI 30 m, 0.250 mm, 0.25 μ m, capillary column using Ultra-pure 6.0 helium as the carrier gas maintained at a constant flow of 1 ml/min. The sample was introduced in splitless mode with a purge time of 1 min. The oven temperature was maintained at 70°C for 2 min and then programmed to increase to 150°C at 30°C/min and then to 310°C at 4°C/min, where it was held isothermally for 10 min. Detection was performed by a single-quadrupole mass spectrometer (Agilent 5973) using EI⁺ mode. The mass spectrometer was operated under selective ion monitoring (SIM) mode with two or three ions per target PAH or deuterated PAH. A calibration curve was prepared by serially diluting the standard solutions to prepare 6 calibration standards of increasing concentrations: 25 μ g/L, 50 μ g/L, 100 μ g/L, 500 μ g/L, 1,000 μ g/L, 3,000 μ g/L. The internal standard, p-Terphenyl-d14 was introduced by serially diluting the stock solution to yield a concentration of 1000 μ g/L. The obtained quadratic calibration equations (all $R^2 > 0.99$) were then used to quantify the unknown samples. Concentrations are reported in nanograms per gram of initial dry weight (5.0000 g) powdered-rock (ng/g dw). The serially diluted EPA 525 PAH Mix A

was used as an initial calibration verification standard (ICVS), allowing a percent recovery ranging from 80-120%. Analysis of the method blank demonstrated that the analytical system and glassware were free of contaminants (Appendix 6B). Additionally, analysis of the fortified blank established the efficacy of the extraction and separation method with an average percent recovery of 101% for the primarily targeted analytes (perylene, chrysene and phenanthrene) (Appendix 6B). Furthermore, analysis of the fortified sample showed that influence from matrix-induced bias was not an issue for the targeted analytes (Appendix 6B). Surrogate average recovery calculated from all samples for the three primary deuterated analytes (perylene-d12, chrysene-d12 and phenanthrene-d10) were 100%, 103% and 77%, respectively.

6.3.6 Correlation Analysis

Correlation coefficients were determined for various proxies using Microsoft Office Excel 2013. The correlation coefficient is based on the Pearson's r equation (1896) expressed as:

$$\text{Correl (X, Y)} = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

Where $\bar{x}$ and $\bar{y}$ are the corresponding sample's average. The results of this equation vary from a perfect negative correlation (-1), no correlation (0) to a perfect positive correlation (1). Values in between will be labeled as: 0.1-0.3 = weak, 0.4-0.6 = moderate, 0.7-0.9 = strong.

6.4 Results

6.4.1 Lithology and Fossil Content

In the field, the El Pujal section generally occurs as a scarp slope topography, cut by obsequent streams that allow easy exposure of the rock sequence of the present study

(14.29 m – 85.04 m) (Fig. 6-1D, E). The outcrop is composed of a repetitive series of differentially weathered packets of indurated beds that are followed by soft, more easily weathered beds. The surficial gray (N6) to medium dark gray (N4) coloration of the beds is unvarying throughout but vanishes with depth to the unweathered rock into a grayish black (N2) hue. The lower 25 m (14.29 m – 39.29 m) includes a repetitive series of soft/hard beds with a flaky-fissile weathered surface yet having excellent consolidated condition once the unweathered level is reached below the surface. This sequence intergrades with a 21.15 m-thick (39.29 m – 60.44 m) well-indurated rock series, and the uppermost 24.7 m (60.44 m – 85.14 m) of the succession shows a recurrence of the lithology similar to the lower 25 m, but with more extended levels of the softer interbeds between 72.03 m and 85.04 m (Fig. 6-2I). Identifiable macrofossils are absent throughout the section, except for occasional unidentifiable ferruginous clumps (~ 3 – 4 mm) and pyritized burrow fillings.

At the microscopic scale changes are inconspicuous revealing a monotonous matrix, however subtle textural and allochem variations are detectable as summarized in photomicrographs of Figure 6-2. Thin section analysis reveals a uniform, kerogen-rich micritic matrix with dispersed pyrite and allochems that rarely exceed 30% as the hallmark of this interval of the studied El Pujal section. Pyrite is common in less indurated samples and less frequent in more lithified beds (Fig. 6-2R, S). Pyrite grains appear disseminated throughout the samples with framboids infilling burrows and bioclasts, especially benthic foraminifera. Typical bioclasts include benthic and planktic foraminifera (Fig. 6-2A, B, C, D, E, F, G, L, N), echinoid fragments (Fig. 6-2H, I, J), rare ostracods (Fig. 6-2K), roveacrinid fragments (Fig. 6-2M) and rare small sized (300 - 800

Figure 6-2 I) Simplified lithostratigraphic column depicting the distribution of various lithologies in this 70.75 m-interval covering from 14.29 m to 85.04 m of the El Pujal section. Points marked with an X represent intervals where *Leupoldina Cabri* specimens are present. II–III) Time series counts of benthic foraminifera and echinoid fragments. IV) Bioturbation index following the proposed scheme in Taylor and Goldring (1993). Greenish bands correspond to argillaceous limestone and marlstone intervals. A–S) Thin section images of common microfossils and fragments as well as the rock matrix found throughout this study, scale at 200 μ m. A–F) Images of representative *Leupoldina cabri* from El Pujal. G) Image of a planktonic foraminifera with chambers partly infilled with pyrite. H) Image of an echinoid spine cut perpendicular to axis. I–J) Images of a large echinoid fragment and spine. K) Image of an ostracod valve. L) Image of a benthic foraminifera with pyritized chambers. M) Images of roveacrinid fragments found throughout this interval. N) Image of an *Ammodiscus* benthic foraminifera. O–Q) Images of minute gastropods and bivalve generally found in marlstone layers. R) Image of a representative limestone sample, with high bioturbation (BI = 6). S) Image of a representative marlstone sample with low bioturbation (BI = 3) and abundant pyrite.

μ m) bivalves and gastropods (Fig. 6-2O, P, Q) mostly occurring in marlstone intervals.

Temporal occurrences of bioclasts vary throughout, but benthic foraminifera ρ and echinoid fragments ρ yield the smallest concentrations at the levels corresponding to marlstone and argillaceous limestones (Fig. 6-2II, III). The bioturbation index (BI) varies between 3 and 6, with minimum values correlative with intervals with the lowest benthic fauna ρ (Fig. 6-2IV).

The index taxon *Leupoldina cabri* was first identified in the El Pujal sequence in the basal portion of the section at a stratigraphic height of 13.77 m (Socorro and Maurrasse, 2019), and other specimens (e.g. Fig. 6-2A, B, C, D, E, F) are further identified in this interval (14.29 m – 85.04 m) where it occurs at least in 25 samples of the studied section (Fig. 6-2I noted with an X).

6.4.2 TIC/TOC/ $\delta^{13}\text{C}_{\text{org}}$

Carbon geochemistry results for this 70.75 m interval of the El Pujal section are shown in Appendix 6D and Figure 6-3 as follows:

TIC concentrations yield an average of 69.86% with the lowest value of 54.92% at 75.93 m and the highest of 81.46% at 20.14 m. As previously explained (section 6.3.2), three distinct lithologies are recognized based on the range of TIC values, namely limestones, argillaceous limestones and marlstones (Fig. 6-3A). TIC values (Fig. 6-3B) starting at stratigraphic level 14.29 m oscillate above and below the average of 70% up to 46.65 m. Succeeding TIC values increase above the average over an interval of 13.69 m ending at 60.34 m. Above this level the values begin to fluctuate again within a 24.7 m-interval where they remain primarily below the average ($\bar{x} = 64.08\%$), except at the levels of two limestone layers at 63.67 m and 72.03 m, respectively (Fig. 6-3B). In general, TIC has a moderate positive correlation with benthic fauna ρ , whereby higher benthic foraminifera

ρ ($r = 0.64$) and echinoid fragment ρ ($r = 0.57$) occur in limestone layers (Fig. 6-2I, II, III). A similarly moderate correlation occurs between TIC and BI ($r = 0.69$) with higher values in limestone layers, and lower values as low as 3 occurring in marlstone layers (Fig. 6-2IV).

The TOC record (Fig. 6-3C) displays an inverse ($r = -0.76$) pattern to that recorded by the TIC curve. Values fluctuate throughout with an average of 1.07%, reaching a minimum of 0.41% at 72.03 m and a maximum of 1.83% at 75.22 m. The lower 24.37 m-interval (14.29 m – 38.66 m) exhibits a fluctuating pattern mostly above average. By contrast, the succeeding 21.68 m (38.66 – 60.34 m) transitions into values that drop below the average. The overlying 11.69 m-interval, between 60.34 m and 72.03 m, yields TOC values oscillating below and slightly above the average. The end point reaches the lowest value of the studied section, but on the whole this interval yields higher values than the subjacent interval. The remainder (~ 13 m) of the studied section shows another relative increase in TOC values consistently above the average ($\bar{x} = 1.42\%$) while TIC dips inversely below the average (Fig. 6-3B, C). Also, variations in TOC inversely correlate with fluctuations in benthic foraminifera ρ ($r = -0.56$) and echinoid ρ ($r = -0.51$), (Fig. 6-2II, III) whereby these benthic organisms are less frequent in intervals of argillaceous limestones and marlstones, higher in TOC values. A similar inverse relationship occurs between TOC and BI values ($r = -0.68$), which are lower in intervals of higher organic carbon concentration.

The $\delta^{13}\text{C}_{\text{org}}$ values measured on the bulk organic fraction fluctuate throughout the studied section around an average of $\sim -24.02\text{‰}$ (Fig. 6-3D) and within a range of 1.65‰, from a minimum of -25.09‰ to a maximum value of -23.44‰ . The lower part of

Figure 6-3 A-D) Stratigraphic variation of carbon geochemical data compared with lithology. Vertical red dashed line represents the average value of the respective variable. Greenish bands correspond to argillaceous limestone and marlstone intervals. E) Relative proportion of terrestrial organic matter derived from a simplified two end-member mixing model utilizing carbon isotope data (refer to discussion).

the studied section (14.29 m - 33.3 m) yields $\delta^{13}\text{C}_{\text{org}}$ values fluctuating above and below the average with a maximum shift of 0.92‰. The following values starting at 33.8 m to 59.27 m (~ 25.47 m) stay predominantly above the average except for a point at 51.52 m where the values decrease to -24.03‰. This interval includes the highest carbon isotope value (-23.44‰) recorded in the studied section at 52.58 m. The upper 25.7 m of the section (59.27 m – 85.04 m), shows a pattern of $\delta^{13}\text{C}_{\text{org}}$ values consistently below the average, and yields the most negative value (-25.09‰) in the sequence at 75.22 m coincident with the highest TOC value (Fig. 6-3C). It is worth noting that the pattern displayed by the $\delta^{13}\text{C}_{\text{org}}$ is somewhat similar to the TIC curve ($r = 0.50$), however the relationship is inverse with TOC ($r = -0.46$). Overall, as illustrated in Figure 6-3, more negative $\delta^{13}\text{C}_{\text{org}}$ values are associated with argillaceous limestone and marlstone intervals that are more enriched in TOC and with lower TIC.

6.4.3 Elemental Analysis

Appendix 6E and Figure 6-4 shows temporal variations of relevant major elemental (Si, Al, Ti) concentrations which vary in concordance throughout the studied section with highest values in marlstones (Fig. 6-4A, B, C, D). Si has the highest concentration ($\bar{x} = 38.97 \text{ ppm} \cdot 10^{-3}$) with values between $20.90 \text{ ppm} \cdot 10^{-3}$ and $66.47 \text{ ppm} \cdot 10^{-3}$, followed by Al ($\bar{x} = 16.35 \text{ ppm} \cdot 10^{-3}$) that fluctuate from a minimum of $9.19 \text{ ppm} \cdot 10^{-3}$ to a maximum of $26.14 \text{ ppm} \cdot 10^{-3}$. Ti exhibits the lowest concentration with an average of $0.67 \text{ ppm} \cdot 10^{-3}$ and values that change from $0.34 \text{ ppm} \cdot 10^{-3}$ to $1.19 \text{ ppm} \cdot 10^{-3}$. In the basal 18.44 m portion of the section (14.0 – 32.44 m), Si, Al, and Ti show a pattern of values that oscillates above and below the average, nearly consistent with the lithological variations. Fluctuations of these elements reach the lowest recorded values in a limestone layer at

32.73 m (Fig. 6-4A, B, C, D) and continue in a similar pattern of variation up to 47.16 m (an interval of ~ 14.43 m). Upward, their values stay generally below the average throughout the limestone until 60.34 m, except for two minor spikes at 52.58 m and 54.7 m, respectively. Above 60.34 m where marlstone interbeds recur more prominently, Si,

Figure 6-4 A-F) Vertical plots of major elements (Si, Al, Ti) and biolimiting elements (Fe, P) compared with lithology. Values in parts per thousand ($\text{ppm} \cdot 10^{-3}$). Vertical red dashed line represents the respective element's average value. Greenish bands correspond to argillaceous limestone and marlstone intervals.

Al, and Ti fluctuations essentially show a distinct trend above the average with the highest values at 75.22 m within the thickest marlstone interbed. Overall, Si, Al and Ti show above average concentrations concurrent with argillaceous limestone and marlstone intervals, whereas limestone intervals tend to have below average concentrations.

Compared with the carbon geochemistry, these major elements show a strong negative correlation with TIC ($r = \text{Si}, -0.92$; $\text{Al}, -0.91$; $\text{Ti}, -0.90$), a moderate positive correlation with TOC ($r = \text{Si}, 0.54$; $\text{Al}, 0.57$; $\text{Ti}, 0.51$) and a moderate negative correlation with

$\delta^{13}\text{C}_{\text{org}}$ for Si ($r = -0.50$) and Ti (-0.56), but a weak negative correlation with Al ($r = -0.38$).

Biolimiting elements (Fe, P) (Fig. 6-4E, F) have a temporal pattern of fluctuation similar to that exhibited by the major elements. Fe shows a strong correlation with Al ($r = 0.87$) with values that vary from $4.58 \text{ ppm} \cdot 10^{-3}$ to $13.52 \text{ ppm} \cdot 10^{-3}$ and average $7.36 \text{ ppm} \cdot 10^{-3}$. P shows a moderate correlation with Al ($r = 0.42$) and its values are lower ($\bar{x} = 0.16 \text{ ppm} \cdot 10^{-3}$) than those recorded for Fe, as they fluctuate between $0.10 \text{ ppm} \cdot 10^{-3}$ and $0.24 \text{ ppm} \cdot 10^{-3}$. For the most part, biolimiting elements tend to be enriched in argillaceous limestone and marlstone layers but have lower values in limestone layers. This relationship is highlighted by the strong negative correlation between TIC and Fe ($r = -0.87$), and the moderate negative correlation of TIC with P ($r = -0.43$). Conversely, intervals of higher TOC show higher concentration of Fe ($r = 0.71$) and P ($r = 0.48$). $\delta^{13}\text{C}_{\text{org}}$ and Fe shows a negative relationship ($r = -0.41$), while P shows a weak negative correlation ($r = -0.12$).

The values for RSTEs (V, Cr, Co, Ni, Cu, Mo and U) analyzed in this study are shown in Appendix 6E and Figure 6-5. Like the previously reported major elements, the RSTEs all show comparable trends throughout the section, with values in the lower 33.41 m (14.29 m – 47.7 m) fluctuating above and below average of each respective element. Above 47.7 m and up to 60.34 m (12.64 m-interval) the limestone shows most RSTE variations within relatively low values (below their respective average), but Cu has an anomalously high peak at 59.27 m, and Mo increases (Fig. 6-5F, G). Above 60.34 m, the

Figure 6-5 A-H) Vertical plots of RSTEs reported as absolute values in parts per million (ppm). I) Vertical plot of RSTEs enrichment indices (EI RSTEs) relative to the Organyà Basin's Average Background Value (OBABV) (for a detailed description refer to the methodology section).

overlying 24.7 m of the studied section is characterized by the highest concurrent RSTE concentrations with maximum values of V (48.24 ppm), Cr (46.48 ppm), and U (1.11 ppm) at 75.22 m in the uppermost marlstone layer. Similarly, Co, Ni, Cu and Mo also show significantly higher values at that same level, although their maximum values occurred in different previous marlstone beds: 25.14 m (Co, 1.44 ppm; Ni, 37.66 ppm); 59.27 m (Cu, 7.68 ppm); and 65.87 m (Mo, 3.06 ppm).

Enrichment Indices (EIs) were calculated for each RSTE in an effort to quantify their fluctuations relative to the Organyà Basin's Average Background Value (OBABV). As shown in Figure 6-5, most RSTEs show peaks coinciding with argillaceous limestone and marlstone intervals, while they shift to lower values in limestone layers. Overall, RSTEs fluctuate close to the average, but only a few elements show enrichments above the OBABV ($EIs > 1$) (Fig. 6-5I, J) and they are mostly correlated with marlstone layers. One such element is V with consistent enrichments above the OBABV in intervals of high TOC ($r = 0.69$) especially at 75.22 m where V content is 1.75 times higher than the background value (Fig. 6-5I). When the EIs are combined ($\sum EIs$) (Fig. 6-5J), the pattern simulates the TOC curve ($r = 0.62$). Conversely, the $\sum EIs$ reflects a strong negative correlation ($r = -0.80$) with TIC, and a moderate negative correlation ($r = -0.45$), with $\delta^{13}C_{org}$. A similar negative affinity is present with benthic foraminifera ρ ($r = -0.53$), echinoid fragment ρ ($r = -0.67$) and BI ($r = -0.60$).

6.4.4 Clay Mineralogy

Results of the clay mineral analyses performed on the $< 2 \mu m$ fraction of seven selected samples representative of the different recurrent lithologies are shown in Figure 6-6. The clay fraction is composed of smectite, illite, kaolinite and chlorite, but is

consistently dominated by illite with percentages between 5% and 70%, and an average of 63%. No apparent association is visible between lithology and illite, whose abundance shares a weak inverse relation with major elemental concentrations, especially Al ($r = -0.22$). Chlorite is the next most abundant clay as it varies between 4% and 19% ($\bar{x} =$

Figure 6-6 Temporal variation in clay mineral content (<2 μm fraction). Selected samples were taken as representative of the various lithologies.

14%) and displays a moderate negative association with lithology (TIC) ($r = -0.49$).

Kaolinite follows with relatively small variability (10% - 14%, $\bar{x} = 12\%$) with the higher percentages associated with argillaceous limestone and marlstone intervals. Smectite

represents the smallest fraction of the clay mineral assemblage and varies between 2% and 23% ($\bar{x} = 11\%$) with higher values in limestone intervals (TIC) $r = 0.42$.

6.4.5 Biomarkers

Total lipid extracts (TLE) yielded color variations ranging from grayish yellow (5Y 8/4), moderate yellow (5Y 7/6) and moderate olive brown (5Y 4/4) (Fig. 6-7VI).

Regardless of extract color intensity, all samples display a bright, light blue (5B 7/6) fluorescence under both long- and shortwave UV radiation (Fig. 6-7VI). Color variations in TLE show a relationship with lithology whereby lighter, grayish yellow extracts are associated with low TOC of the limestone intervals; moderate yellow extracts mainly coincide with argillaceous limestone intervals; and the darkest, moderate olive brown extracts correspond with high TOC, marlstone layers.

Biomarker analysis of the aliphatic portion focused on *n*-alkanes, hopanes (m/z 191) and steranes (m/z 217, m/z 218, m/z 259). Figure 6-8 (A-E) shows values obtained for different biomarker parameters. In Figure 6-8E the aliphatic fraction of the studied samples reveals a very low unresolved complex mixture hump (UCM) and is dominated by *n*-alkanes and the acyclic isoprenoids pristane (Pr) and phytane (Ph). The *n*-alkanes display an asymmetric range between nC_{10} and nC_{37} with a general unimodal positively skewed distribution. Estimated relative input of terrestrial vs aquatic OM input or Terrestrial Aquatic Ratio (TAR) (Bourbonniere and Meyers 1996) were calculated from the results of the 64 samples analyzed and plotted in Figure 6-8D. TAR ($nC_{27} + nC_{29} +$

$nC_{31}/(nC_{15} + nC_{17} + nC_{19})$ values average 0.27 owing to the predominance of shorter chain *n*-alkanes (nC_{15} , nC_{17} , nC_{19}) over the relatively less abundant longer chain

Figure 6-7 I-V) Plots of analyzed PAHs compared with lithology and TOC. VI) Coloration of total lipid extract compared with lithology (I) and TOC (II). Letters A-H next to the TOC curve (II) correspond to letters under images in VI showing images taken under ambient light and both, short wave and long wave UV light. Notice the intensity in lipid coloration varies with lithology and TOC content, with darker yellow extracts in argillaceous limestone and marlstone/higher TOC intervals and lighter yellow extracts in limestone/lower TOC intervals.

Figure 6-8 A-D) Comparison between lithology and various organic geochemical proxies. E) Representative total ion chromatograms of the aliphatic fraction from the three lithologies. The large peaks in the chromatograms are mainly a homologous series of n-alkanes. Labeled peaks refer to n-alkane's carbon chain length for reference purposes. Peaks labeled as Pr and Ph refer to pristane and phytane, respectively.

homologs (nC_{27} , nC_{29} , nC_{31}). When compared with lithologic variations the general trend shows higher TAR values associated with argillaceous limestone and marlstone intervals, while lower values occur in limestone layers. In addition, TOC displays a positive correlation ($r = 0.28$) with TAR values, whereas higher TAR values concur with intervals of lowest $\delta^{13}C_{org}$ values ($r = -0.53$). As shown in Table 6-2 the longer chain ($>nC_{24}$) n -alkanes show no odd-to-even predominance with an average OEP (2) of 1.01 (OEP (2)),

Table 6-2 List of biomarker thermal maturity parameters, their corresponding sample number and stratigraphic position.

Sample ID	Height (m)	Ts/(Ts+Tm)	$C_{31} 22S/(22S+22R)$	$C_{29} 20S/(20S+20R)$	$C_{29} \beta\beta/(\beta\beta+\alpha\alpha)$
C-16-138	75.22	0.74	0.56	0.46	0.63
C-16-135	72.03	0.79	0.58	0.48	0.67
C-16-120	54.7	0.64	0.58	0.45	0.64
C-16-65	25.14	0.72	0.60	0.44	0.62
C-16-54	19.66	0.69	0.54	0.46	0.61
<hr/>					
CPI_{avg}	$OEP(2)_{avg}$				
1.05	1.01				

after Scalan and Smith, 1970), and an average carbon preference index (CPI) of 1.05

(CPI, after Bray and Evans, 1961). Both OEP (2) and CPI show no correlative variations with lithology (for a complete list of values refer to Appendix 6C). Among the isoprenoids, pristane to phytane ratios (Pr/Ph) range from a low of 1.91 to a maximum value of 3.13 and an overall average of 2.55. Values of Pristane/ n - C_{17} and Phytane/ n - C_{18} are relatively low as they average 0.32 and 0.13, respectively. A plot of Pristane/ n - C_{17} vs Phytane/ n - C_{18} (Fig. 6-9A) shows most samples fall within the mixed type II/III kerogen, and some plotting towards the upper boundary into the terrigenous type III kerogen area.

The hopanoids (m/z 191 chromatograms) show a similar distribution pattern, but with varying proportions depending on lithology. In general, the studied samples are dominated by C_{30} hopane and C_{29} norhopane, 18α -22,29,30-trisnorneohopane (Ts), 17α -

Figure 6-9 A) Cross plot of Pristane/n-C₁₇ vs. Phytane/n-C₁₈ of selected samples. Fields after Shanmugam (1985) from concepts proposed by Lijmbach (1975). B) Ternary diagram showing the sterane composition of selected samples and their relationship with source. Fields after Shanmugam (1985) from concepts proposed by Huang and Meinschein (1979).

22,29,30-trisnorhopane (Tm) and the extended hopanes or homohopanes (C₃₁-C₃₄) (Fig. 6-10, Table 6-3). The Ts/(Ts+Tm) ratio ranges from 0.64 to 0.79, averages 0.72 (Table 6-2) and shows no particular relationship with lithology. Homohopanes show a distribution from C₃₁ to C₃₄, whereby C₃₁>C₃₂>C₃₃>C₃₄. The C₃₁ and C₃₂ 22S/(22S+22R) homohopane isomerization ratio yields average values of 0.57 and 0.60, respectively. Gammacerane is also present in all the samples where it is usually found eluting just after the C₃₁ (22R) homohopane isomer. A plot of the gammacerane index (gammacerane/C₃₁R-homohopane) shows a general trend with higher values, up to 1.21 in marlstone intervals and lower values (0.58) in limestone intervals (Fig. 6-8C).

Regular steranes and diasteranes occur in all the studied samples ranging from C₂₇ to C₂₉ (Fig. 6-10, Table 6-3). The samples are characterized by having relatively high percentages of 5 α ,14 α ,17 α (H) (20R) C₂₇ ($\bar{x}$ = 34.59%) and 5 α ,14 α ,17 α (H) (20R) C₂₉ regular sterane (αααR) ($\bar{x}$ = 34.02%), but more moderate values of 5 α ,14 α ,17 α (H) (20R) C₂₈ regular sterane ($\bar{x}$ = 31.39%). A ternary diagram of αααR C₂₇%, αααR C₂₈%, and

Figure 6-10 A) Trace chromatograms of a representative sample showing the relative distribution of hopanes (m/z 191), steranes (m/z 217 and 218) and diasteranes (m/z 259). For peak identification, refer to Table 6-3. B-1-3) Total ion chromatograms of the aromatic fraction from representative samples of marlstone (C-16-138), limestone (C-16-120) and argillaceous limestone sample (C-16-47) showing the relative abundance of perylene.

$\alpha\alpha\alpha R$ $C_{29}\%$ shows that the samples plot in the general area of estuarine to open marine OM (Fig. 6-9B). A plot of the ratio of $5\alpha,14\alpha,17\alpha(H)$ (20R) C_{27} to $5\alpha,14\alpha,17\alpha(H)$ (20R) C_{29} (C_{27}/C_{29}) reveals values as low as 0.82 for marlstone layers and much higher values, up to 1.24 in a limestone bed at 54.7 m (Fig. 6-8B). Isomerization of the C-20 stereocenter in the $5\alpha,14\alpha,17\alpha(H)$ C_{29} regular sterane given as the 20S/(20S+20R) ratio

Table 6-3 Various biomarker compounds. The numbers are used for compound assignment in Figure 6-10A.

Hopanes (<i>m/z</i> 191)	Steranes (<i>m/z</i> 217 and 218) and Diasteranes (<i>m/z</i> 259)
1. 18 α -22,29,30-Trisnorhopane (Ts)	17. C ₂₇ 13 β ,17 α (H) diasterane (20S)
2. 17 α -22,29,30-Trisnorhopane (Tm)	18. C ₂₇ 13 β ,17 α (H) diasterane (20R)
3. C ₂₉ 17 α ,21 β (H) hopane	19. C ₂₈ 13 β ,17 α (H) diasterane (20S)
4. 18 α -30-norhopane (29Ts)	20. C ₂₈ 13 β ,17 α (H) diasterane (20R)
5. C ₃₀ diahopane ?	21. C ₂₉ 13 β ,17 α (H) diasterane (20S)
6. C ₃₀ 17 α ,21 β (H) hopane	22. C ₂₇ 5 α ,14 α ,17 α (H) sterane (20R)
7. C ₃₀ 17 β ,21 α (H) hopane ?	23. C ₂₇ 5 α ,14 β ,17 β (H) sterane (20S)
8. C ₃₁ 17 α ,21 β (H) homohopane (22S)	24. C ₂₉ 13 β ,17 α (H) diasterane (20R)
9. C ₃₁ 17 α ,21 β (H) homohopane (22R)	25. C ₂₈ 5 α ,14 α ,17 α (H) sterane (20S)
10. C ₃₀ Gammacerane	26. C ₂₈ 5 α ,14 β ,17 β (H) sterane (20S)
11. C ₃₂ 17 α ,21 β (H) homohopane (22S)	27. C ₂₈ 5 α ,14 α ,17 α (H) sterane (20R)
12. C ₃₂ 17 α ,21 β (H) homohopane (22R)	28. C ₂₉ 5 α ,14 α ,17 α (H) sterane (20S)
13. C ₃₃ 17 α ,21 β (H) homohopane (22S)	29. C ₂₉ 5 α ,14 β ,17 β (H) sterane (20R)
14. C ₃₃ 17 α ,21 β (H) homohopane (22R)	30. C ₂₉ 5 α ,14 β ,17 β (H) sterane (20S)
15. C ₃₄ 17 α ,21 β (H) homohopane (22S)	31. C ₂₉ 5 α ,14 α ,17 α (H) sterane (20R)
16. C ₃₄ 17 α ,21 β (H) homohopane (22R)	

ranges from 0.44 to 0.48 with an average of 0.46 (Table 6-2). Similarly, beta-isomerization at C-14 and C-17 in the 5 α ,14 α ,17 α (H) C₂₉ 20S and 20R regular sterane given as the C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio or 5 α ,14 β ,17 β (H) C₂₉ (20S+20R) / (5 α ,14 β ,17 β (H) C₂₉ (20S+20R) + 5 α ,14 α ,17 α (H) C₂₉ (20S+20R)), ranges from 0.61 to 0.67 with an average of 0.64 (Table 6-2).

Three aromatic fractions from samples representative of the three principal lithologies were analyzed because they yielded the yellow color variations and fluorescence previously described. Analysis by full-scan GC/MS reveals that marlstone and argillaceous limestone samples contain elevated concentrations of the pentacyclic aromatic hydrocarbon, perylene (Fig. 6-10B-1, B-3). In contrast, a similar chromatogram from a limestone bed representative sample, displays a relatively depressed perylene peak (Fig. 6-10B-2).

Further analysis of the aromatic fraction focused on the quantification of PAHs. Of particular interest was the concentration of perylene and other PAHs such as chrysene

and phenanthrene, which were detected in significant concentrations and their results, are reported in Appendix 6B. As presented in Figure 6-7III, the concentration of perylene varies from 747 to 3,365 ng/g dw with an average value of 1,733 ng/g dw. The concentration of perylene was higher in an argillaceous limestone (sample: C-16-85: 1,577 ng/g dw) and in marlstone intervals ($\bar{x}$ = 2,788 ng/g dw), but lower in limestone intervals ($\bar{x}$ = 757 ng/g dw). Similarly, the concentration of chrysene fluctuates with lithologies between 325 and 3,812 ng/g dw (Fig. 6-7IV) ($\bar{x}$ = 1,712 ng/g dw: limestone: $\bar{x}$ = 399 ng/g dw; argillaceous limestone: 1,851 ng/g dw; marlstone: $\bar{x}$ = 2,957 ng/g dw). Relatively high concentrations of phenanthrene were also detected with values ranging from 89 ng/g dw to 5,654 ng/g dw (Fig. 6-7V) and an average of 2,219 ng/g dw. Much like perylene and chrysene, phenanthrene values follow lithologic variations (limestone: $\bar{x}$ = 114 ng/g dw; argillaceous limestone: 2,882 ng/g dw; marlstone: $\bar{x}$ = 3,992 ng/g dw).

6.5 Discussion

6.5.1 Biomarker Interpretations: Thermal Maturity

Thermal maturity concerning OM-rich sedimentary rocks is a measure of the degree of heat-driven reactions generally associated with burial, which converts OM to kerogen, petroleum, gas and graphite (Curiale et al., 1989; Peters et al., 2005; 2007). Thermal maturity assessment based on molecular parameters has become common practice in most geochemical studies used as a critical tool similar to conventional methods (e.g. Rock-Eval pyrolysis, vitrinite reflectance) (Peters et al., 2007). Evaluating thermal maturity through biomarker analysis relies on the essential principle of structural modification of compounds from a precursor molecule with biological functions to a thermodynamically stable, molecular fossil (Curiale et al., 1989). In the following, we

discuss the reliability of the different parameters applicable to evaluate the potential OM thermal maturity of the different lithologies in the 70.75 m continuing study of the El Pujal section.

One of the simplest molecular-based maturity parameters is the relative abundance of odd versus even carbon numbered *n*-alkanes, CPI, or OEP (2) (e.g. Peters et al., 2005; 2007). This parameter relies on the observation that unaltered lipids derived from terrestrial plant OM yield a predominance of odd over even numbered *n*-alkanes because they can produce a reaction that builds a complex with two-carbon units three times to obtain six, which is then split in half to yield three. Thus, the CPI, or OEP (2) values are significantly above 1. Thermal degradation brings OEP (2) values close to unity (Bray and Evans, 1961; Eglinton and Hamilton, 1967). The relatively low values for CPI (1.05) and OEP (2) (1.01) recorded in the El Pujal section would thus imply thermally mature OM (Table 6-2). However, the reliability of either CPI or OEP(2) as a strict thermal maturity parameter remains debatable because it can also be affected by a number of factors, including OM source, as well as the environmental conditions in which the source vegetation grew (Luo et al., 2012; Bush and McInerney, 2013; Stroeve et al., 2013; Huang et al., 2016; Zhao et al., 2018a).

Thermal maturity can be further assessed based on the relative thermodynamic stability difference between C₂₇ hopanes, particularly the more stable 18 α -22,29,30-trisnorhopane (Ts) and the less stable 17 α -22,29,30-trisnorhopane (Tm) (Kolaczowska et al., 1990). This parameter is reportedly more reliable and is commonly represented as the Ts/(Ts+Tm) ratio, whose value increases up to a maximum of 1 as Tm is completely exhausted during advanced stages of thermal maturation (Peters et al.,

2007). The results obtained for the studied samples yield $T_s/(T_s+T_m)$ values consistently <1 , with an average of 0.72 (Table 6-2), which again suggests that the OM experienced noticeable thermal stress. However, the $T_s/(T_s+T_m)$ ratio is also not strictly controlled by thermal maturity, it can be altered depending on variable sources of OM, as well as the presence of clay minerals (McKirdy et al., 1983; Moldowan et al., 1986; Peters et al., 2007). These factors thus constrain the effective use of the $T_s/(T_s+T_m)$ ratio to the evaluation of thermal maturity of lithologies with low clay content and consistent OM sources, prerequisites which are not met for the El Pujal sequence.

Arguably, perhaps the most reliable thermal maturity indicators applicable to the El Pujal rocks are those resulting from isomerization reactions involving the hydrogen atoms at the C-22 position in the homohopane (C_{31} - C_{35}) homolog series (Curiale et al., 1989; Peters et al., 2007). At the C-22 chiral center, the biological form of these homohopanes carry a 22R configuration, which during thermal alteration converts to the 22S epimer (Curiale et al., 1989; Peters et al., 2007). The ratio of 22R to 22S, often calculated as $22S/(22S+22R)$, can be determined for all of the C_{31} - C_{35} homohopanes (Peters et al., 2007), but the C_{31} -homohopane is typically the ratio used since variations in the ratio of homopanes C_{32} to C_{35} could occur with higher homologs (Zumberge, 1987; Köster et al., 1997; Pan et al., 2008). The $22S/(22S+22R)$ ratio rises from 0, ultimately reaching a value of approximately 0.6 at equilibrium (Seifert and Moldowan, 1986; Peters et al., 2007). In the El Pujal section, the C_{31} homohopane $22S/(22S+22R)$ ratio varies from 0.54 to 0.60 and has an average value of 0.57 (Table 6-2), which indicates that the samples have probably not exceeded a thermal maturity equivalent to an early stage of the oil window ($\sim 50^\circ\text{C}$)(Peters et al., 2007). Similarly, isomerization of certain

steranes can also be used as thermal maturity indicators. Isomerization at the C-20 position in the $5\alpha,14\alpha,17\alpha(H)$ C₂₉ regular sterane shifts from an exclusive 20R configuration in biologically derived steroid precursors to a 20S epimer during thermal alteration (Curiale et al., 1989; Peters et al., 2007). The 20S/(20S+20R) C₂₉ regular sterane ratio for the El Pujal section yielded values that range from 0.44 up to 0.48 with an average of 0.46 (Table 6-2). Since these values are below the equilibrium value of ~ 0.52-0.55, they also corroborate that OM in the section reached thermal conditions nearing the early oil window (Seifert and Moldowan, 1986; Peters et al., 2007). In addition, the $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio of C₂₉ 20R and 20S regular steranes caused by the isomerization of asymmetric centers at the C-14 and C-17 positions is another parameter used as a maturity indicator. The C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio changes from 0 to an equilibrium value of ~ 0.67-0.71 with increasing thermal maturity (Seifert and Moldowan, 1986; Peters et al., 2007). The El Pujal section has C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$ values of 0.61 to 0.67 with an average of 0.64, below the calculated equilibrium values. Once more, the values of this thermal proxy concur with the previous criteria indicating that that OM in the different lithologies reached temperatures not exceeding the early oil window (Peters et al., 2007). The consistency between the biomarker thermal maturity indicators (e.g. plot of C₂₉ 20S/(20S+20R) vs C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$) (Fig. 6-11) with values below equilibrium endpoints indicate that the sediments probably experienced mild temperatures of ~ 50°C to 60°C, equivalent to the onset of oil generation. The results permit to deduce that thermal over maturity can be ruled out when interpreting the organic geochemical results of the El Pujal section; hence, as a corollary the preserved biomarker data presumably characterizes the original signals with minor to no alteration.

Figure 6-11 Plot of $C_{29} 20S/(20S+20R)$ vs $C_{29} \beta\beta/(\beta\beta+\alpha\alpha)$ thermal maturity indicator values for selected samples. Dashed lines indicate equilibrium values.

6.5.2 Biomarker Interpretations: Biological Source Evaluation

n-Alkanes are straight chain alkanes or the simplest of a class of organic compounds biosynthesized by a variety of organisms, from microbial phytoplankton of marine and fresh water environments to terrestrial plants. Lipid extracts from extant organisms reveal that frequently shorter chain *n*-alkanes ($nC_{14} - nC_{19}$) dominate in microbial phytoplankton, while aquatic macrophytes and *sphagnum* species (peat moss) are enriched in nC_{20} to nC_{25} , and higher plants have longer chains ($>nC_{25}$), derived from leaf epicuticular waxes (Eglinton and Hamilton, 1967; Han et al., 1968; Winters et al., 1969; Gelpi et al., 1970; Blumer et al., 1971; Cranwell, 1984; Viso et al., 1993; Riederer and Markstädter, 1996; Baas et al., 2000; Ficken et al., 2000; Mead et al., 2005; Koch et al., 2009; Schirmer et al., 2010; Gao et al., 2011). These characteristic differences in carbon chain length produced by various organisms make the distribution of *n*-alkanes in sediments an effective proxy for determining OM sources (Cranwell, 1973; Giger et al., 1980; Meyers, 1997; Forster et al., 2004; Peters et al., 2005; 2007; Brocks and Summons, 2014). The general distribution of *n*-alkanes in the El Pujal section (Fig. 6-8E) ranges from nC_{10} to nC_{37} , with a positive skew and dominance of mid to short-chain ($\leq nC_{25}$) homologs. Hence, these *n*-alkanes reflect a mixed OM source, dominantly derived from

microbial phytoplankton and aquatic macrophytes, with a relatively minor, but still noticeable input from terrestrial higher plants. The plot of the values of Pristane/ n -C₁₇ vs Phytane/ n -C₁₈ (Fig. 6-9A) show that most samples fall within the mixed type II/III kerogen indicative of marine and terrestrial environments, thus lending further support to the original source provided by the n -alkane chain lengths. Nonetheless, given the possible constraint associated with the use of this ratio because heterotrophic bacteria generally degrade the more labile n -alkanes before the isoprenoids, our interpretation relies on the fact that the UCM hump is almost non-existent in the chromatograms, which indicates that biodegradation is at least minimum (Wenger and Isaksen, 2002; Peters et al., 2005).

The n -alkane data imply that the OM pattern of mixed origin recorded in the El Pujal lithologies is compatible with typical continental margin environments where sediments archive a complex OM signal with influence from distinct interconnected ecosystems that include rivers, estuaries and the ocean system itself (Méjanelle and Laureillard, 2008; Ramaswamy et al., 2008; Carreira et al., 2010; Schmidt et al., 2010; Bauer et al., 2013; Cordeiro et al., 2018). The present results also concur with previous works in the Organyà Basin (García-Senz, 2002; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro and Maurrasse, 2019). While the range of the n -alkanes distribution in the chromatograms reveals clues on the various sources of OM supplied to the basin in the studied interval, it does not permit a clear conclusion concerning significant temporal variability with the lithologies because most chromatograms show only subtle differences (Fig. 6-8E). A more distinct delineation emerges when we used the TAR to estimate the relative input of terrestrial vs aquatic OM

by comparing the relative abundances of short (nC_{15} , nC_{17} , nC_{19}) and long (nC_{27} , nC_{29} , nC_{31}) chain length n -alkanes (Bourbonniere and Meyers 1996; Meyers, 1997). The TAR temporal trend shows variation with lithologies (Fig. 6-8D), with elevated values associated with argillaceous limestone and marlstone beds concurrent with peaks in TOC, whereas lower values are in limestone layers. A possible explanation for higher TAR in beds with greater TOC values may be related to the labile characteristics of the type of chain length associated with the source OM. For instance, studies of modern open ocean environments of the Pacific have shown that degradation of plankton-derived OM only allows $\sim 0.1\%$ to 1% of the OM produced in the epipelagic zone to reach the seafloor, and only $\sim 0.01\%$ actually accumulates in the sediment (e.g. Hernes et al., 2001). In the case of the Organyà Basin, the long-chain homologs having more recalcitrant properties were probably more readily preserved, thus an increase of terrestrially-derived OM with more resistant qualities may explain their higher relative concentration in beds with greater amount of preserved TOC (Cranwell, 1981; Kawamura et al., 1987; Meyers and Eadie, 1993; Meyers, 1997; Hernes et al., 2001). In fact, higher Si, Al, and Ti content (Fig. 6-4) concurrent with stronger terrestrial biomarker signatures in the OM-rich beds supports enhanced fluvial pulses as the principal delivery system of these long chain n -alkanes to the basin (e.g. Hedges et al., 1997; Schefuß et al., 2004; Schmidt et al., 2010; Schreuder et al., 2018).

The general phylogenetic specificity of certain steranes makes them also a viable proxy for OM source identification. For instance, while prokaryotic organisms use particular types of hopanoids in their cell walls, all eukaryotic cell walls, particularly the outer membrane, include abundant specific types of sterols. Diagenetic alteration of

sterols produce steranes as a class of tetracyclic triterpanes (Nes, 1974; Mackenzie et al., 1982; Moldowan et al., 1985; Hartmann, 1998; ; Méjanelle et al., 2000; Schaller, 2003; Volkman, 2003, 2005; Peters et al., 2005; Dufourc, 2008). Commonly, red algae and zooplankton show elevated values of C₂₇ sterols, phytoplankton (green algae, coccolithophores, diatoms) and some fungi are dominated by C₂₈ sterols, while OM derived from terrestrial plants have higher concentrations of C₂₉ sterols (Huang and Meninshein, 1979; Volkman, 1986; Sailot et al., 1991; Volkman et al., 1998; Volkman, 2003; Peters et al., 2005). In the El Pujal section, the presence of regular steranes ($\alpha\alpha\alpha$ R) at averages of C₂₇ (34.59%), C₂₈ (31.39%), and C₂₉ (34.02%), further suggests a mixed input of OM from various eukaryotic organisms. A ternary diagram (Fig. 6-9B) of the relative abundances of C₂₇, C₂₈, and C₂₉ $\alpha\alpha\alpha$ R steranes shows that the samples plot in the general area of estuarine to open marine OM. These results lend support to the complex nature of OM preserved in the semi-restricted Organyà Basin which accumulated hemipelagic sediments typically derived from both allochthonous terrestrial sources and autochthonous marine sources, consistent with the evidence obtained from the *n*-alkanes distribution (Sikes et al., 2009; Zhang et al., 2014a; O'Reilly et al., 2014). A lithologic relationship also occurs similar to that discussed for the *n*-alkanes. Higher proportion of C₂₉ $\alpha\alpha\alpha$ R relative to C₂₇ $\alpha\alpha\alpha$ R (C₂₇/C₂₉) (Fig. 6-8B) is recorded in marlstone beds in further agreement attesting to heightened input of terrestrially-derived plant OM during these intervals. Because these intervals also coincide with higher TAR values together with peaks in Si, Al and Ti, thus the sterane record underscores the influence of increased fluvial fluxes associated with deposition of these beds. By comparison with possible modern analogs, perhaps the modern-day East China Sea (ECS) may represent a

corresponding environment since it is reported that the Cháng Jiāng (Yangtze) River delivers higher amount of C₂₉ sitosterol and stigmasterols during the spring and summer wet seasons (Kim et al., 2016; Duan et al., 2017).

At El Pujal, the approximate duration of the increased terrigenous influence on sedimentation in the Organyà Basin can be estimated using the average thickness of ~ 3.3 m for the argillaceous limestone and marlstone beds. Assuming the highest sedimentation rate of 7.5 cm/ky calculated by Sanchez-Hernandez et al, (2014) for earlier deposits also applies at this younger level, these beds translate approximately to 44 kyrs. These intervals with increased terrigenous input therefore indicate that enhanced riverine discharge in the Organyà Basin lasted with frequencies that approach the known Milankovitch cycle (period ~ 41,000 years) associated with changes in the obliquity of the earth's axis of rotation (e.g. Hays et al., 1976). Similar duration of regional climatic effects related to insolation-driven forcing of intensified continental runoff have been demonstrated in the Mediterranean area during the latest Miocene (Mayser et al., 2017) and the Pleistocene last interglacial (Wu et al., 2018).

The presence of hopanes, the altered and saturated version of hopanoids, provide useful information on prokaryotic contribution to the preserved OM in the section. Hopanoids are a class of pentacyclic triterpenoids found in the lipid membrane of various prokaryotes, including aerobic-heterotrophic bacteria, anaerobic sulfate-reducing bacteria, and cyanobacteria (Ourisson et al., 1979; 1982; 1987; Ourisson and Rohmer, 1992; Sinninghe Damsté et al., 2004; Härtner et al., 2005; Blumenberg et al., 2006; Peters et al., 2007). Since these hopanoids contain a rigid, amphiphilic structure similar to that of sterols, thus they have comparable structural roles in cells of prokaryotic organisms as

sterols do in eukaryotic cells (Rohmer et al., 1979). The hopanoids in these bacterial membranes such as bacteriohopanetetrol are biochemically derived from the complex cyclization reaction of squalene precursors (Kannenberg and Poralla, 1999). The diagenetic derivatives of hopanoid lipids are pentacyclic triterpanes containing between 27 to 35 carbon atoms commonly referred to as hopanes (Peters et al., 2007). The presence of hopanes in all the studied samples thus implies that bacteria were also an important source of OM input in the sediments. In addition, all the samples show elevated levels of gammacerane, a non-bacterially derived compound, seen eluting after the C₃₁ (22R) homohopane isomer (Fig. 6-10A, Table 6-3). Gammacerane contributes to further our understanding of the biotic factors involved in the supply of OM into the basin because its known precursor is the triterpenoid alcohol, tetrahymanol (gammaceran-3 β -ol) generated through various biochemical mechanisms originating from freshwater and marine ciliates feeding on anaerobic bacteria (Mallory et al., 1963; Venkatesan, 1989; Ten Haven et al., 1989; Harvey and Mcmanus, 1991; Sinninghe Damsté et al., 1995; Harvey et al., 1997; Peters et al., 2007). Usually, these ciliates incorporate sterols derived from a sterol-rich algal diet in their membranes. When their diet is deprived of sterols, they feed on heterotrophic bacterial communities and begin to replace certain sterols in their membranes with tetrahymanol (Conner et al., 1968, 1971; 1982). This is especially true of marine ciliates when they are allowed to feed on natural bacterial communities (Harvey et al., 1997). In modern environments, bacterivorous ciliates occur at the aerobic/anaerobic interface of stratified water columns where chemoautotrophic and purple sulfur bacteria thrive (Zubkov et al., 1992; Guhl and Finlay, 1993; Sinninghe Damsté et al., 1995; Sass et al., 2001; Lin et al., 2006). Therefore, the occurrence of

gammacerane in the El Pujal samples further provides compelling biomarker evidence of stratification of the water column at that time in corroboration of previous studies of earlier development of the Organyà Basin (Sanchez-Hernandez and Maurrasse, 2014; 2016; Socorro and Maurrasse, 2019). Moreover, temporal variation in gammacerane expressed as the gammacerane index (Fig. 6-8C), with relatively high values up to 1.21 in marlstones and lower values (0.58) in limestones, reveals persistent stratification of the water column.

In summary, the temporal distribution pattern of the biomarkers (Fig. 6-8) concur with the terrestrially derived elements (Si, Al, Ti) (Fig. 6-4) of the studied section to indicate the influence of periodic intensified riverine fluxes on the origin of the sedimentary organic matter.

6.5.3 Polycyclic Aromatic Hydrocarbons (PAHs) Distribution: Paleo-implications and their Potential as Geochemical Proxies

During the total lipid extraction (TLE) phase for biomarker analysis, a curious relationship between lithology and extract coloration was observed, whereby lighter grayish yellow (5Y 8/4) extracts were associated with low TOC limestones, whereas moderate yellow (5Y 7/6) extracts coincided with argillaceous limestones, and the darkest, moderate olive brown (5Y 4/4) extracts, corresponded with high TOC marlstones (Fig. 6-7VI). Preliminary GC/MS analysis conducted on the aromatic fractions of a representative sample from each of the three lithologies yielded a pronounced late-eluting perylene peak (Fig. 6-10B-1, B-2, B-3) in concordance with the yellow coloration and the vivid blue fluorescence (Fig. 6-7VI) characteristic of this compound (Forster et al., 2004).

The pattern of variable temporal presence of perylene in the sediments thus prompted for further investigation of its origin and significance in the Organyà Basin.

Perylene is a five-membered ring PAH ($C_{20}H_{12}$) that commonly occurs under a wide range of recent environments, including marine (Orr and Grady, 1967; Wakeham et al., 1979; Soclo et al., 2000; Dahle et al., 2003; Hu et al., 2014; Kumar et al., 2017); lacustrine (Wakeham et al., 1980; Tan and Heit, 1981; Soma et al., 1996; Silliman et al., 1998; Bakhtiari et al., 2009; Itoh and Hanari, 2010; Fan et al., 2011), and fluvial settings (Hites et al., 1980; Countway et al., 2003; Yunker and Macdonald, 2003; Liu et al., 2008). Perylene has also been found in peat, coal (Bergmann et al., 1964; Shan-Tan and Kaplan, 1992; Bechtel et al., 2007), crude oils (Golovko et al., 1999; Scarlett et al., 2019), ancient sediments, and rocks (Louda and Baker, 1984; Baker and Louda, 1986; Garrigues et al., 1988; Venkatesan, 1988; Jiang et al., 2000; Hasegawa, 2001; Forster et al., 2004; Grice et al., 2009; Suzuki et al., 2010; Romero-Sarmiento et al., 2011; Zhang et al., 2014b). Perylenequinone pigments are recognized as the most probable precursor of perylene, and they are largely produced by wood-degrading fungi (Sato, 1976; Griffith and Boddy, 1991; Jiang et al., 2000; Bechtel et al., 2007; Grice et al., 2009; Itoh and Hanari, 2010; Suzuki et al., 2010; Itoh et al., 2012; Marynowski et al., 2013) under very humid conditions (Gilbertson, 1980; Harris, 2001). In most cases perylene exhibits a strong positive relationship with terrestrial OM proxies (Aizenshtat, 1973; Countway et al., 2003; Bertrand et al., 2013; Varnosfaderany et al., 2014; Zhang et al., 2014b), or is directly found in terrestrial material such as peat bogs and fungi-degraded wood (Malawska et al., 2002, 2006; Bechtel et al., 2007; Jiang and Liu, 2008; Marynowski et al., 2013). Some studies have postulated that perylene is from land-derived biological

precursors, while others have argued that different perylenequinone pigments (e.g. 4,9-dihydroxyperylene-3,10-quinone) are the most probable precursors, because of their structural similarities with perylene (Orr and Grady, 1967; Kumada, 1988; Jiang et al., 2000; Itoh et al., 2012). Because perylene is usually found associated with anoxic sediments and is absent, or present only in low concentrations in oxic surface sediments (Choudhary and Routh, 2010) its occurrence also indicates that reducing conditions are involved in its depositional processes, since quinone compounds are sensitive to oxidation (Orr and Grady, 1967; Aizenshtat, 1973).

The perylene concentration in each of the selected El Pujal samples (Fig. 6-7III) revealed a variable pattern linked with lithology: values are higher in argillaceous limestones (1,577 ng/g dw) and marlstones ($\bar{x}$ = 2,788 ng/g dw) than in limestones ($\bar{x}$ = 757 ng/g dw). Also, significant positive correlation exist between perylene and the major elements Al, Si and Ti (r = 0.87, 0.84, 0.86), which is in accord with evidence from biomarker proxies (TAR, C_{27}/C_{29}) that show a strong relationship (r = 0.90, -0.88) between periods of intensified land-derived OM influx and elevated perylene concentration. Concurrence of these data for the El Pujal section thus provides robust evidence to suggest fluvial transport of land-based OM as the main pathway to supply perylene and /or its biogenic precursors to the Organyà Basin. This assumption is in agreement with modern findings that revealed high perylene abundances in soils (Krauss et al., 2005; Gocht et al., 2007) and in suspended river particles (Luo et al., 2006; Varnosfaderany et al., 2014). The lithological and biomarker characteristics of the El Pujal succession concur that periodic higher riverine discharges delivered increased soil and/or woody debris from forests and wetlands during inundation (Robertson et al., 1999;

Hilton et al., 2012). Conditions at that time were, perhaps, analogous to the episodic flow and flood pulses (Junk et al., 1989) characteristic of large modern river systems such as the Amazon (e.g. Fisher and Parsley, 1979; Hedges et al., 1986; Junk et al., 1989; Richey et al., 1989; Quay et al., 1992; Junk, 1997; Dunne et al., 1998; McClain et al., 2001; Moreira-Turcq et al., 2003; 2013; Clark et al., 2013). Given that the source of perylene precursors are essentially from terrestrially-derived plant OM of humid climates (e.g. Baldrian and Valášková, 2008; Varnosfaderany et al., 2014), its occurrence in the El Pujal sediments implies a humid climate in the Organyà Basin region during OAE1a. Our data thus confirm previous studies to suggest that perylene may also be used as a dependable proxy of moist and humid continental paleoclimatic conditions (Suzuki et al., 2010; and references herein). Additionally, because the formation of perylene may involve reducing conditions, its highest concentrations (Fig. 5I, Fig. 7III) in marlstones coeval with RSTEs enrichments above the OBABV lends evidence for some degree of recurring reducing conditions related to enhanced riverine discharges of terrestrial OM (Orr and Grady, 1967; Aizenshtat, 1973; Garrigues et al., 1988).

Chrysene ($C_{18}H_{12}$, composed of four fused benzene rings) and phenanthrene ($C_{14}H_{10}$, composed of three fused benzene rings) were also found in relatively high concentration (chrysene up to 3,812 ng/g dw; phenanthrene up to 5,654 ng/g dw) in the same samples that contain perylene. These PAHs are recognized to be widespread constituents of crude oils, coal tar and rock extracts that contain remains of OM (Borrego et al., 1997; Li et al., 2012; Gross et al., 2015; Kashirtsev et al., 2018). Some studies have suggested a diagenetic origin of chrysene from hopanes by cleavage of ring-E and successive aromatization from ring-D to ring-A (Borrego et al., 1997), or by cleavage of

ring-A and successive aromatization from ring-A to ring-D (Laflamme and Hites, 1979). The distribution pattern of chrysene is concomitant with perylene ($r = 0.99$), which also suggests a connection to a terrestrial precursor. Since chrysene can form from hopanes, whose precursors are hopanoids found in the lipid membrane of various bacteria (Ourisson et al., 1979; 1982; 1987; Ourisson and Rohmer, 1992; Sinninghe Damsté et al., 2004; Härtner et al., 2005; Blumenberg et al., 2006; Peters et al., 2007), its presence suggests that intervals of intermittent intensified input of land-derived nutrients (Fe, P) (Fig. 6-4E, F) increased *in-situ* primary productivity which heightened heterotrophic bacteria activities.

Similarly, phenanthrene has been reported to be genetically related to steroids found in non-specific biological source material (Mair, 1964; Greiner et al., 1976; Tissot and Welte, 1984). Given that prevalent humid conditions existed at that time in the area, it is possible that the hygrophilous Hepaticae, which contains large numbers of phenanthrenes (Adam and Becker, 1993; Flegel et al., 1999; Rycroft et al., 1999), are potential source of the precursors. Indeed, the Hepaticae originated in the Ordovician (Wellman et al., 2003), and are reported to have flourished in the Lower Cretaceous (Cantrill, 1997; Limarino et al., 2012; Diéguez et al., 2007; Mendes et al., 2018).

6.5.4 Significance of Small-sized Mollusks in OM-rich Layers Versus Riverine Fluxes

In addition to their distinct geochemical characteristics, the OM-rich marlstones also include unusually high concentration of microscopic bivalves ($\bar{x} \sim 200 \mu\text{m}$) and gastropods ($\bar{x} \sim 300 \mu\text{m}$) (Fig. 6-2O, P, Q). These microscopic shells reccur in the Organyà Basin deposits during the time interval under study as well as in the older basal

13.77 m portion of the El Pujal section (Socorro and Maurrasse, 2019). Their steady small size is of interest because they have apparent similarities in size and morphologies to pteropod shells, but these pelagic mollusks can be ruled out because their known first fossil occurrence is in the middle to late Campanian (Janssen and Goedert, 2016; Janssen and Peijnenburg, 2017). Instead, these minuscule shells are comparable to those found associated with immature veliger larvae of mollusk bivalves and gastropods (Boué and Chanton, 1962). The micro mollusk shells occur exclusively in OM-rich marlstone beds together with gammacerane, a proxy indicative of a well-stratified water column at that time in the Organyà Basin (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro and Maurrasse, 2019). Thus, their presence in sediments with elevated values of Si, Al and Ti (Fig. 6-4B, C, D), concomitant with increased inputs of terrestrial OM (Fig. 6-8B, D) and nutrients, establishes their relationship with recurrent heightened riverine fluxes. Hence, these microscopic shells may be interpreted to represent remains of molluscan planktonic larvae that flourished intermittently during wet climatic conditions conducive to unusual molluscan larval production. Such scenario is compatible with the *n*-alkane results for these intervals yielding significant mid-chain length compounds (*n*C₂₀-*n*C₂₅) characteristic of aquatic macrophytes (Cranwell, 1984; Viso et al., 1993; Ficken et al., 2000; Mead et al., 2005; Gao et al., 2011) and *sphagnum* species (Baas et al., 2000). The influence of this type of vegetation is evident in the estuarine OM signature recorded in the ternary plot of % C₂₇, % C₂₈, % C₂₉ $\alpha\alpha\alpha$ R steranes (Fig. 6-9B). Additional evidence in support of this assumption is found in uppermost Barremian riverine/estuarine deposits of similar age found approximately 30 miles southwest of the El Pujal section in the Montsec chains, which contain abundant

Montsechia, a primitive aquatic angiosperm (Selden and Nudds, 2012; Gomez et al., 2015). Accordingly, the vegetal fossil record in the adjacent area also demonstrates that *sphagnum* species and aquatic angiosperms were common in the region in the Early Cretaceous and may have played a major role in the supply of OM to the Organyà Basin.

6.5.5 Factors Involved in OM Production and Preservation

The conditions required for the accumulation of OM-rich sediments have been extensively debated in the literature. One of the primary factors is a supply of OM generated either *in-situ* by enhanced surface productivity in the photic zone or through a combination of local productivity and fluvial transportation of terrestrial OM to the marine realm (Suess, 1980; Deuser, 1988; Pedersen and Calvert, 1990; Hedges et al., 1997). Minor amount may also reach the marine environment by aeolian processes (Gagosian et al., 1981; 1986; 1987; Schreuder et al., 2018). However, productivity alone may not be sufficient, as it has been estimated that generally under normal oceanic conditions only approximately 0.1% - 1% of the OM produced in the upper water column reaches the seafloor (Hernes et al., 2001; Middelburg and Meysman, 2007). Therefore, in order to increase OM preservation, factors such as reducing conditions with less efficient anaerobic degraders (Demaison and Moore, 1980; Canfield, 1994), rapid burial, grain size, and types of clays also control OM protection. Given that preservation of OM is a complex, multivariable process, unique features of each basin must be taken into account when examining the predominant factors involved in their origin (Suess, 1973; Tanoue and Handa, 1979; Mayer, 1994; Keil et al., 1994a, 1994b; Hedges and Keil, 1995; Bergamaschi et al., 1997; Ransom et al., 1997; Satterberg et al., 2003; Kennedy et al., 2002, 2014).

In the El Pujal section, substantial amount of preserved OM ($\bar{x} = 1.07\%$) occurs throughout the interval under study (14.29 m – 85.04 m) with peaks reaching up to 1.83% (Fig. 6-3C). Since the biomarkers are dominated by shorter chain *n*-alkanes ($\leq nC_{19}$), they indicate that the bulk of the OM was produced in the basin (Fig. 6-8E). As the short chain *n*-alkanes suggest, primary productivity may have been fueled by relatively high concentrations of biolimiting Fe ($\bar{x} = 7.36 \text{ ppm} \cdot 10^{-3}$) and P ($\bar{x} = 0.16 \text{ ppm} \cdot 10^{-3}$) (e.g. Hart, 1934; Martin and Fitzwater, 1988; Martin et al., 1990, 1994; Krom et al., 1991; de Baar et al., 1995; Zohary and Robarts, 1998; Boyd et al., 1999, 2000; Diaz et al., 2001; Gervais et al., 2002; Coale et al., 2004; Blain et al., 2007; Moore et al., 2009). The presence of gammacerane distinctive of stratification in the basin, and a lack of siliceous microfossils such as radiolaria imply that upwelling was not a controlling mechanism for the delivery of the critical biolimiting nutrients to the epipelagic zone. Since the temporal distribution of major elemental concentrations parallels that of Fe and P (Fig. 6-4), these critical nutrients were, therefore, apparently supplied together with terrigenous materials via fluvial fluxes sourced from the weathering of crystalline terranes and apatite-bearing Variscan rocks in the watershed (García-Alcade et al., 2002; Ábalos et al., 2002; Sanchez-Hernandez et al., 2014). Moreover, because the presence of perylene concurs adequately with other proxies that imply a humic-rich catchment area was associated with the Organyà Basin, Fe chelation with soil humic and fulvic acids is an alternative pathway for its delivery into the basin. In fact, these chelation complexes are water soluble and allow Fe to be transported from fluvial waters offshore where siderophore ligands released by microorganisms and photodegradation greatly enhances its

bioavailability (Batchelli et al., 2010; Nieto-Cid et al., 2006; Laglera and van den Berg, 2009; Kuhn et al., 2014; Krachler et al., 2015, 2019).

Intensified biological productivity also produces largely labile OM (Romankevich, 1984; Tissot and Welte, 1984) which may lead to enhanced bacterial degradation and to oxygen-deprived conditions. In fact, intervals of marlstones and argillaceous limestones higher in TOC (Fig. 6-3A, C) reflect some level of oxygen deficiency because they yielded relatively lower benthic faunal counts, lower bioturbation index and higher concentration of pyrite (Fig. 6-2). RSTE values (Fig. 6-5) compared with benthic fauna δ (Fig. 6-2II, III) also show trends in agreement with fluctuating low oxygenation level in the basin as peaks in these elements coincide with intervals depleted in benthic organisms. Similarly, bioturbation index (BI) and RSTEs exhibit a largely inverse relationship, as indicated by the moderate negative correlation between V and BI ($r = -0.57$). RSTE values are characteristically lower within intervals with high TIC/low TOC (limestone layers), and more elevated within those with low TIC/high TOC (argillaceous limestones and marlstones). This relationship is further demonstrated by the strong negative correlation between V and TIC ($r = -0.92$) and moderate positive correlation with TOC ($r = 0.69$). Overall, RSTE enrichments beyond the background natural value shown in Figure 6-5 are synchronous with high TOC, consistent with previously discussed oxygenation proxies. Of particular interest is the constant enrichment of V and Cr above the OBABV at intervals associated with peaks in TOC, especially in the lowermost 10.85 m (14.29 m - 25.14 m), and the uppermost part of the section. Considering that V and Cr are the most easily reduced of the RSTEs, their fluctuating enrichment only at these levels substantiate weakly oscillating reducing conditions

(Calvert and Pederson, 1993; Li et al., 2015). The absence of RSTE enrichments in the succeeding limestone interval (47.16 m – 60.34 m), which also contains relatively low TOC ($\bar{x}$ = 0.83 %), signifies a time of improved oxygenation, inducing higher rate of remineralization of the marine snow, hence reducing export production. By contrast, the uppermost 24.70 m of the section (60.34 m – 85.04 m) comprises again OM-rich argillaceous limestones and marlstones with simultaneous enrichments of most RSTEs above the OBABV yielding peaks up to 1.75 times the background natural value as recorded at 75.22 m (Fig. 6-5I, J). Concurrence of RSTE enrichments with these OM-rich intervals thus provides robust evidence that stronger reducing conditions dominated during the deposition of these beds and contributed to OM preservation. The biochemical processes controlling the amount of OM recorded in the sediments of the Organyà Basin at that time can thus be summarized as resulting from a combination of enhanced OM production associated with terrigenous fluxes supplying biolimiting elements together with abundant land-derived OM. Preservation was influenced by decreased remineralization due to exacerbated oxygen deficiency related to poor vertical mixing of a stratified water body.

In addition to the factors discussed above, as peaks in TOC are associated with argillaceous and marlstone beds which correlate well with major elements, especially Al (r = 0.57) derived from clays, OM preservation must have also involved physicochemical processes related to the enclosing minerals. XRD analysis conducted on the clay fraction (< 2- μ m) reveals illite as the predominant clay mineral ($\bar{x}$ = 63%) (Fig. 6-6). OM protective sorption is activated onto mineral grains especially clays with high surface areas (Hedges and Keil, 1995), and surface reactivity, unique to its composition. By this

process ~ 90% of the total sedimentary OM from various marine settings cannot be physically separated from its mineral matrix (Hedges and Keil, 1995). Since illite contains exposed Al-OH groups that act as amphoteric points (Eslinger and Pevear, 1988), it is capable of binding negatively and/or positively charged polar organic compounds, physically encapsulating the OM and preventing bacterial degradation (Chen et al., 2018). Other organic compounds without polar functional groups, such as *n*-alkanes, may also bond to clay minerals through Van der Waals and hydrogen bonding (Keil and Mayer, 2014). In addition to illite, the fraction consisting of smectite ($\bar{x}$ = 11%), kaolinite ($\bar{x}$ = 12%) and chlorite ($\bar{x}$ = 14%) (Fig. 6-6) has been demonstrated to show strong affinity to dissolved organic matter associated with phytoplankton biomasses, thereby improving their preservation potential (Satterberg et al., 2003). Besides the physicochemical processes associated with clay minerals, simple increase of suspended sediment loads causing rapid burial is another preservation factor that enhances the export of OM to the sediment by decreasing its exposure time to rapid remineralization.

The OM preserved in the El Pujal section may have also experienced different preservation potentials because of their various sources (Haddad et al., 1992). The biomarker data associated with the OM-rich beds yielded higher proportion of C₂₉ to C₂₇ regular steranes and higher TAR values implying an increase in terrestrially-derived OM (Fig. 6-8B, D), which consists essentially of recalcitrant, nitrogen-free compounds like lignin, cutin and cellulose. These kinds of OM are stable because they have already undergone extensive biological and abiological degradation from source to sink (Cummins and Klug, 1979; De Leeuw and Largeau, 1993; Meyers, 1997). They are often

bound to clay minerals that result from soil forming processes, hence becoming inaccessible to microbes and thereby increasing their preservation potential as compared to the readily accessible OM generated *in-situ* (Volkman et al., 1981; Haddad et al., 1992; Meyers and Ishiwatari, 1993; Santos et al., 1994; Jaffé et al., 2001; Holtvoeth et al., 2010).

6.5.6 Chemo/Biostratigraphic Correlation

Results of numerous studies of Lower Cretaceous sequences coeval with OAE1a have established correlation in the long-term patterns of variations in carbon isotopic values ($\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$) which have also been integrated in a robust stratigraphic framework (Menegatti et al., 1998; Dumitrescu and Brassell, 2006; Moullade et al., 1998, 2015; Westermann et al., 2013; Gaona-Narvaez et al., 2013a; Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2016; Naafs et al., 2016). The established records of carbon isotope data can, therefore, be used not only as an effective correlation tool (e.g. Scholle and Arthur, 1980; Weissert, 1989; Weissert and Bréhéret, 1991; Menegatti et al., 1998; Herrle et al., 2004; Jarvis et al., 2015), but also as a proxy to recognize changes in the global carbon reservoir associated with major crises (Jarvis et al., 2015) that affected both marine and non-marine environments (Gröcke et al., 1999; Ando et al., 2002).

The high sediment accumulation rate in the Organyà Basin (Sanchez-Hernandez et al., 2014) generated an expanded archive that documents continuous changes that permit high-resolution chemostratigraphic studies of OAE1a. Hence, the carbon isotopic data of the Organyà Basin have revealed details of the carbon isotope segments identified with OAE1a not disclosed elsewhere (Fig. 6-12) (e.g. Menegatti et al., 1998; García-Senz,

2002; Sanchez-Hernandez et al., 2014; Aguado et al., 2014a; Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro et al., 2017). The present results (70.75 m-portion) of the El Pujal section complement two previous carbon isotopic curves obtained for segment C1 through the early part of C5 from the El Pui section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) and the lower 14 m at El Pujal (Socorro and Maurrasse, 2019). The combined $\delta^{13}\text{C}_{\text{org}}$ data extended at El Pujal show a pattern consistent with the positive plateau equated to segment C5 and its characteristic short-lived positive spike (Fig. 6-12, point marked with a star) (Socorro and Maurrasse, 2019). Furthermore, the high-resolution $\delta^{13}\text{C}_{\text{org}}$ data enables us to establish in details the variations of segment C5, beginning with the positive peak recorded at 211.40 m within the El Pui section (Fig. 6-12F), which differentiates the end of segment C4. The composite curve (Fig. 6-12F) shows a greatly expanded segment C5 starting at El Pui. The upwards extension into the El Pujal section (Fig. 6-12F) permits to subdivide segment C5 into six subsegments. The first subsegment (C5-a) starts at El Pui with a value of -23.68‰ at 211.40 m and extends over 16.90 m revealing an overall slight negative trend ending at 228.30 m with a value of -24.60‰. Subsegment C5-b records a pronounced positive shift of 2.05‰ from 228.30 m at El Pui up to the maximum value of -22.55‰ recorded at a stratigraphic height of 0.55 m correlated in the El Pujal section (Fig. 6-12F, point marked with a star). Upward subsegment C5-c, $\delta^{13}\text{C}_{\text{org}}$ values progress stepwise to a minimum of -24.54‰ at 26.81 m. In subsegment C5-d the curve fluctuates over a total of 25.77 m, displaying a general positive trend up to a value of -23.44‰ at 52.58 m. Subsegment C5-e extends over 22.64 m (52.58 m – 75.22 m) and shows a progressive decrease in values to a minimum of -25.09‰ at 75.22 m. The final

Figure 6-12 A-E) Chemostratigraphic correlation based on $\delta^{13}\text{C}_{\text{org}}$ of the El Pujal section (Socorro and Maurrasse (2019) and this study) with La Frontera (Aguado et al., 2014a,b), Roter Sattel (Menegatti et al., 1998), Cison (Menegatti et al., 1998) and El Pui (Sanchez-Hernandez and Maurrasse, 2016). The C segments correspond to the subdivisions proposed by Menegatti et al. (1998). The yellow star marks the highest value within segment C5 and corresponds to equivalent points in each section. The gray band indicates the position of OAE1a or its equivalent for each section. F) Plot of El Pui and El Pujal $\delta^{13}\text{C}_{\text{org}}$ data with identical vertical and horizontal scales. For a detailed description of labeled subsegments C5-a through C5-f refer to the discussion section.

subsegment (C5-f) spans from 75.22 m to 85.04 m, but this interval may include only the initial portion of an overextended C5 because the end of that segment includes a pronounced negative inflection identifiable in sequences elsewhere that is still lacking in the El Pujal data (Fig. 6-12A, B, C). We infer that forthcoming additional $\delta^{13}\text{C}_{\text{org}}$ data in progress in the section will help clarify, and likely disclose the negative shift (e.g. La Frontera (Fig. 6-12A) (Aguado et al., 2014 a, b); Roter Sattel, and Cismon sections (Menegatti et al., 1998) (Fig. 6-12B, C).

Recent biostratigraphic results from lower Aptian successions are in agreement that the occurrence of the index planktonic foraminifer, *L. cabri* parallels the stratigraphic interval that includes OAE1a (Magniez-Janin et al., 1997; Aguado et al., 1999; Bellanca et al., 2002; Verga and Premoli Silva 2002; Erba, 2004; Coccioni et al., 2006; Heldt et al., 2008; Moullade et al., 2015). The presence of *L. cabri* throughout the El Pujal section (Socorro and Maurrasse, 2019) (Fig. 6-2I, marked with an X) further corroborates the chemostratigraphic correlation with OAE1a (Fig. 6-12).

6.5.6.1 Regional Influence on the Distribution of $\delta^{13}\text{C}$ values of TOC

The general structure of the $\delta^{13}\text{C}_{\text{org}}$ curve at El Pujal reveals a pattern comparable to the global signature of segment C5 in other sections elsewhere (Fig. 6-12), albeit small regional modulating influences. The minor $\delta^{13}\text{C}_{\text{org}}$ variations in the expanded succession are of particular importance with regards to fluxes of *in-situ* vs allochthonous OM discussed above, as distinct organisms are known to produce different $\delta^{13}\text{C}_{\text{org}}$ values (Burns and Beardall, 1987; Raven and Johnston, 1991; Ehleringer et al., 1993). It is well established that the $\delta^{13}\text{C}_{\text{org}}$ values of terrestrial C-3 plants are more negative (typically -26‰ to -28.5‰) (Bender, 1971; Boutton, 1991; Dawson et al., 2002; Fry, 2006; Kohn,

2010) than OM produced in the open ocean (generally $\sim -21\text{‰}$) (Wainright and Fry, 1994). Based on these distinct characteristics we attempt to determine the extent of modulation of the $\delta^{13}\text{C}_{\text{org}}$ values due to the effects of the OM source on the data. The $\delta^{13}\text{C}_{\text{org}}$ values show a moderate negative relationship with TOC ($r = -0.46$), with essentially more negative values associated with argillaceous limestone and marlstone beds. Since increases in TAR and higher proportion of C_{29} $\alpha\alpha\alpha\text{R}$ sterane relative to C_{27} $\alpha\alpha\alpha\text{R}$ sterane ($\text{C}_{27}/\text{C}_{29}$) (Fig. 6-8B, D) demonstrate the influence of elevated inputs of terrestrial OM in these intervals, then the regional modulating effect on the $\delta^{13}\text{C}_{\text{org}}$ curve produced by variable OM sources becomes apparent.

To estimate the relative contribution of terrestrial and marine OM in the TOC, the carbon isotope data was used as the basis of a simplified two end-member mixing model (e.g. Calder and Parker, 1968; Shultz and Calder, 1976; Minoura et al., 1997; Schlünz et al., 1999; Hu et al., 2006; Ramaswamy et al., 2008; Xu et al., 2017; Cordeiro et al., 2018).

The equation used:
$$T_{\text{om}}\% = \frac{\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{org}}}{\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{terrestrial}}} \times 100$$

Where $T_{\text{om}}\%$ is the percent terrestrial organic carbon, $\delta^{13}\text{C}_{\text{org}}$ is the measured $\delta^{13}\text{C}_{\text{org}}$ of an individual sample, $\delta^{13}\text{C}_{\text{terrestrial}}$ is the $\delta^{13}\text{C}_{\text{org}}$ value of the local terrestrial end member, and $\delta^{13}\text{C}_{\text{marine}}$ is the $\delta^{13}\text{C}_{\text{org}}$ value of the marine end member. The terrestrial end member at El Pujal was taken as -25.09‰ from a marlstone sample at stratigraphic height 75.22 m, because it includes the lowest $\delta^{13}\text{C}_{\text{org}}$ value recorded in this interval and simultaneously yielded the highest terrestrial OM input previously discussed with the biomarkers. The marine end member was taken as -23.44‰ from a limestone sample at 52.58 m which has the most positive $\delta^{13}\text{C}_{\text{org}}$ value recorded in this interval and coincides with one of the

lowest TAR values. Concordance of these parameters should reflect the closest value of marine OM. The results from the end-member mixing model are presented in Figure 6-3E where distinct trends in temporal OM distribution concerning the different lithologies are in accord with other proxies. Note that the results using this approach are approximate, because of the absence of authentic end member $\delta^{13}\text{C}_{\text{org}}$ values for terrestrial vegetation and marine OM.

6.5.7 Clay Mineralogy vs Paleoclimatic Signals

A relatively high percentage of illite compared with other clays (Fig. 6-6) characterizes the El Pujal rocks. The lack of variability with depth suggests that illite concentration represents the source composition rather than diagenetic effects (Weaver, 1958). As the condition of thermal maturity from biomarker data suggests, the sediments experienced temperatures equivalent to the onset of oil generation ($\sim 50^{\circ}\text{C} - 60^{\circ}\text{C}$), which is too low to initiate smectite illitization (Cuadros and Linares, 1996; Kübler and Jaboyedoff, 2000; Du et al., 2019). The high abundance of illite may find its source from low grade terranes of mica-rich metamorphic rocks related to the Hercynian orogeny that are abundant in the Pyrenees (Guitard, 1970; Wickham et al., 1987). Illite also lacks correlation with lithology, which implies that its concentration represents the constant background clay mineral input from terrigenous fluxes of the adjacent eroding landmasses. By contrast, smectite increases in limestones while kaolinite is prevalent in marlstones (Fig. 6-6), which suggests that their variation is mostly controlled by the modulating effects of weathering processes (Biscaye, 1965; Griffin et al., 1968; Singer, 1984; Eslinger and Pevear, 1988; Chamley, 1989; Weaver, 1989; Bühmann and Schoeman, 1995). Here, kaolinite and smectite are interpreted as products of soil

weathering under pulses of contrasting climate regimes, humid versus dry, respectively (Weaver, 1989; Wilson, 1999). Chlorite concentration also varies with lithology as higher values occur in marlstones relative to limestones (Fig. 6-6). Co-variation of kaolinite and chlorite seems to be inconsistent because these two clay minerals form under dissimilar conditions (Chamley, 1989). Their simultaneous occurrences therefore suggest two distinct sources, from the mechanical weathering of low-grade metamorphic terranes in the headwater catchment areas, while kaolinite originated from mature soils that likely developed in the watersheds. Thus, periods of enhanced fluvial discharge associated with a more humid climate are also reflected in the deposition of argillaceous limestone and marlstone intervals with higher kaolinite and chlorite content.

6.6 Conclusions

The El Pujal section of the Organyà Basin provided the opportunity for a high-resolution geochemical study of a unique expanded hemipelagic facies of continuous sediment accumulation. The results of the multiproxy study on a continuous 70.75 m portion of the section reveal intricate details archived in the sediments as specific responses of the basin to perturbations of the global carbon cycle associated with OAE1a.

- Deposits during the studied interval consist of a repetitive sequence of limestones, argillaceous limestones and marlstones with varying proportions of OM, carbonate and siliciclastic materials indicative of changing hydrologic conditions.
- New biomarker evidence of reliable sterane (C_{29} 20S/(20S+20R) and C_{29} $\beta\beta$ /($\beta\beta$ + $\alpha\alpha$)) and hopane (C_{31} 22S/(22S+22R)) thermal maturity indices with values below equilibrium endpoints suggest that sediments probably experienced mild temperatures of $\sim 50^{\circ}\text{C}$ to 60°C , equivalent to the onset of oil generation. Thermal over maturity

can thus be ruled out when interpreting the organic geochemical results of the El Pujal section. Therefore, the preserved organic geochemical data characterizes the original signals with minor to no alteration.

- The presence of *n*-alkanes ranging from nC_{10} to nC_{37} regular steranes ($\alpha\alpha\alpha R$) at averages of C_{27} (34.59%), C_{28} (31.39%), and C_{29} (34.02%) and hopanes in all the studied samples demonstrates a mixed source of OM from *in-situ* primary production, bacteria, aquatic macrophytes and terrestrial vegetation. The relative abundances of C_{27} , C_{28} , and C_{29} $\alpha\alpha\alpha R$ steranes shows that the samples plot in the general area of estuarine to open marine OM. The results lend support to the complex nature of OM preserved in the semi-restricted Organyà Basin that derived from both autochthonous marine sources and allochthonous sources including aquatic macrophytes from coastal estuaries and terrestrial vegetation that likely flourished in the floodplain of rivers and streams that emptied into the Basin. Also, elevated levels of gammacerane in all the samples provides compelling biomarker evidence of stratification of the water column at that time in corroboration of previous studies of earlier development of the Organyà Basin. The stratigraphic distribution of the biomarkers coincides with the terrestrially derived elements (Si, Al, Ti) to indicate the influence of periodic intensified riverine fluxes on the origin of the sedimentary organic matter.
- Appraisal of the aromatic lipid fraction revealed elevated concentrations of perylene and a variable pattern with higher values in argillaceous limestones (1,577 ng/g dw) and marlstones ($\bar{x}$ = 2,788 ng/g dw) and lower ones in limestones ($\bar{x}$ = 757 ng/g dw). Concurrence of elevated values of perylene with higher contents of major elements provides robust evidence to suggest fluvial transport of land-based OM as the main

pathway to supply perylene and /or its biogenic precursors to the Organyà Basin.

Considering that the source of perylene precursors are essentially from terrestrially-derived plant OM of humid climates its occurrence in the El Pujal sediments implies a humid climate in the Organyà Basin region during OAE1a. Our data thus confirm previous studies to suggest that perylene may also be used as a dependable proxy of moist and humid continental paleoclimatic conditions. Since the formation of perylene may involve reducing conditions, its highest concentrations in marlstones coeval with RSTEs enrichments lends evidence for some degree of recurring reducing conditions related to enhanced riverine discharges of terrestrial OM.

- The aromatic fraction also revealed relatively high concentrations of phenanthrene, up to 5,654 ng/g dw and chrysene, up to 3,812 ng/g dw, in the same samples that contain perylene. We postulate that the hygrophilous Hepaticae, which contains large numbers of phenanthrenes are potential source of the precursors as they are reported to have flourished in the Lower Cretaceous of the area. In addition, the presence of chrysene that can form from hopanes, whose precursors are hopanoids of bacterial lipid membranes, its presence suggests that intervals of intermittent intensified input of land-derived nutrients (Fe, P) increased *in-situ* primary productivity, which heightened heterotrophic bacteria activities.
- Unusual micro mollusk shells occur only in OM-rich beds together with gammacerane indicative of a well-stratified water column. They are interpreted as remains of molluscan planktonic larvae that flourished intermittently during wet climatic conditions and were likely flushed from adjacent swamps and estuaries, in

- accord with the *n*-alkane results for these intervals yielding significant mid-chain length compounds (*n*C₂₀-*n*C₂₅) characteristic of aquatic macrophytes.
- The biomarkers are dominated by shorter chain *n*-alkanes ($\leq nC_{19}$), thus indicating that the bulk of the OM was produced in the basin. As the short chain *n*-alkanes suggest, primary productivity may have been fueled by relatively high concentrations of critical biolimiting Fe and P. At the same time, RSTE enrichments are coeval with OM-rich intervals, thus providing robust evidence that stronger reducing conditions dominated at these times and contributed to OM preservation. Therefore, preservation was influenced by decreased remineralization due to oxygen deficiency related to poor vertical mixing of a stratified water body. Physicochemical processes associated with clay mineral adsorption, enhanced by recalcitrant OM from terrestrial vegetation and rapid burial were also preservation factors that enhanced the export of OM and their preservation.
 - The combined $\delta^{13}C_{org}$ data extended at El Pujal show a pattern consistent with the positive plateau equated to segment C5 and its characteristic short-lived positive spike, but the studied interval may comprise only part of an overextended C5 because elsewhere the end of that segment includes a pronounced negative inflection that is still lacking in the El Pujal data. The presence of *L. cabri* throughout the El Pujal section also corroborates the chemostratigraphic correlation with OAE1a.
 - Increases in TAR and higher proportion of C₂₉ $\alpha\alpha\alpha$ R sterane relative to C₂₇ $\alpha\alpha\alpha$ R sterane (C₂₇/C₂₉) demonstrate the influence of elevated inputs of terrestrial OM in marlstone intervals, producing a regional modulating effect on the $\delta^{13}C_{org}$ curve due

- to variable OM sources. A two end-member mixing model of terrestrial and marine OM confirms the relationship between TOC and the values of the carbon isotope data.
- Illite is the dominant clay mineral throughout implying steady input from terrigenous fluxes of the adjacent eroding landmasses where it apparently derived from low-grade terranes of mica-rich metamorphic rocks related to the Hercynian orogeny. Periods of enhanced fluvial discharge associated with a more humid climate are also reflected in the deposition of argillaceous limestone and marlstone intervals with higher kaolinite and chlorite content.

The combined results of this study on the 70.75 m portion of the El Pujal section further highlight how the specific responses of a semi-restricted basin modulated the superimposed effects of global forcing factors and determined the fundamental sedimentary expression of OAE1a.

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6.8 References

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6.9 Appendices

Appendix 6A Carlos Herdocia - RSTE values.

Sample ID	Height (m)	V	Cr	Co	Ni	Cu	Mo	U
COR-16-17	35.6	16.41	16.95	1.23	26.30	4.53	4.61	2.76
COR-16-16	32.74	6.87	11.95	0.86	17.34	1.28	1.43	1.24
COR-16-15	31.95	14.44	21.43	0.84	31.61	3.58	3.74	5.53
COR-16-14	29.95	14.34	17.50	1.07	26.02	3.89	12.02	3.35
COR-16-13	27.44	13.32	14.17	0.45	12.44	1.94	1.43	3.27
COR-16-12	23.44	8.97	14.99	0.67	12.77	1.44	0.82	1.63
COR-16-11	17.81	10.15	14.35	0.66	17.43	3.04	2.15	2.11
COR-16-10	14.85	30.54	16.57	1.39	22.19	4.66	14.73	1.27
COR-16-9	10.75	6.59	11.81	0.66	12.16	1.54	1.08	1.35
COR-16-8	7.65	11.88	14.82	0.85	15.76	2.65	3.10	2.27
COR-16-7	6.38	7.67	13.00	0.56	17.49	2.15	1.88	1.10
COR-16-6	4.38	17.56	12.00	0.95	16.30	3.74	5.14	1.26
COR-16-5	3.93	12.45	7.92	0.37	4.20	1.10	0.47	1.61
COR-16-4	1.93	7.65	12.05	0.43	9.89	1.27	1.23	2.00
COR-16-3	0.68	9.93	14.74	0.62	11.24	1.32	1.37	1.54
COR-16-2	0.43	25.31	17.12	0.95	26.87	4.98	12.29	4.26
COR-16-1	0	7.34	18.10	2.19	8.95	1.13	0.69	1.22

*Values in (ppm)

Appendix 6B PAH analysis data.

Analyte	Ion	Sample ID							
		Blank	Fortified Blank	Fortified Sample	C-16-54	C-16-65	C-16-85	C-16-120	C-16-138
Perylene-d12	264	1256	1384	1225	635	796	926	793	1012
Perylene	252	-	937	1760	747	2212	1577	766	3365
Benzo(g,h,i)perylene	276	-	1098	1487	265	508	747	179	1468
Dibenz(a,h)anthracene	278	-	1263	1715	334	343	449	175	864
Indeno(1,2,3-cd)pyrene	276	-	1021	1335	-	-	-	58	-
Benzo(a)pyrene	252	-	1078	1144	-	-	-	-	-
Benzo(k)fluoranthene	252	-	1162	1034	-	-	249	-	-
Benzo(b)fluoranthene	252	-	1073	1309	152	292	308	117	357
Chrysene-D12	240	1271	1392	1325	391	1026	1144	722	954
Chrysene	228	25	1189	1402	325	2102	1851	473	3812
Benzo(a)anthracene	228	48	1126	1167	398	82	89	52	179
Acenaphthene-d10	164	863	587	42	-	58	166	-	47
Fluorene	166	-	873	369	-	56	54	-	151
Acenaphthene	154	-	249	37	-	-	56	-	168
Acenaphthylene	152	-	504	36	-	-	-	-	-
Phenanthrene-D10	188	1254	1168	314	61	918	1232	126	1088
Pyrene	202	-	979	260	30	394	642	40	1151
Fluoranthene	202	-	961	842	-	90	82	-	-
Anthracene	178	-	866	107	-	-	-	-	102
Phenanthrene	178	-	905	499	89	2329	2882	138	5654

*Values in parts per million (ppm)

Appendix 6C Values of calculated biomarker parameters.

Sample ID	Height (m)	CPI	OEP-2	TAR	Pr/n-C ₁₇	Ph/n-C ₁₈	Gammacerane Index	C ₂₇ /C ₂₉	Ts/(Ts+Tm)	C ₃₁ 22S/(22S+22R)	C ₂₉ 20S/(20S+20R)	C ₂₉ ββ/(ββ+αα)
C-16-151	85.04	1.03	1.00	0.35	0.31	0.12						
C-16-146	81.31	0.96	0.87	0.26	0.29	0.13						
C-16-145	80.64	0.92	0.89	0.27	0.32	0.13						
C-16-144	79.55	1.08	1.05	0.31	0.32	0.12						
C-16-143	79.03	1.01	0.97	0.31	0.26	0.11						
C-16-142	78.56	1.02	0.97	0.32	0.24	0.12						
C-16-140	76.78	0.94	0.91	0.27	0.23	0.12						
C-16-138	75.22	1.04	0.99	0.37	0.43	0.20	1.22	0.82	0.74	0.56	0.46	0.63
C-16-137	74.6	0.95	0.90	0.40	0.39	0.21						
C-16-135	72.03	1.05	0.99	0.38	0.32	0.13	0.88	1.15	0.79	0.58	0.48	0.67
C-16-133	69.56	1.08	1.04	0.34	0.46	0.17						
C-16-132	68.3	1.06	1.03	0.32	0.40	0.16						
C-16-130	65.87	1.06	1.01	0.34	0.37	0.17						
C-16-128	63.67	1.06	1.01	0.35	0.36	0.17						
C-16-126	61.51	1.08	1.06	0.34	0.36	0.14						
C-16-125	60.34	1.04	1.01	0.26	0.30	0.11						
C-16-124	59.27	1.08	1.01	0.26	0.27	0.10						
C-16-123	58.15	1.05	1.02	0.33	0.30	0.14						
C-16-121	55.8	0.97	0.89	0.28	0.32	0.14						
C-16-120	54.7	1.10	1.05	0.22	0.33	0.12	0.68	1.24	0.64	0.58	0.45	0.64
C-16-119	54.18	1.08	1.04	0.25	0.34	0.13						
C-16-116	52.58	1.01	0.95	0.21	0.31	0.12						
C-16-114	51.52	1.02	0.96	0.25	0.33	0.15						
C-16-112	50.46	1.05	0.97	0.27	0.29	0.15						
C-16-111	49.85	1.05	1.01	0.27	0.30	0.14						
C-16-109	48.86	1.07	1.01	0.21	0.35	0.14						
C-16-108	48.27	0.98	0.95	0.21	0.29	0.13						
C-16-107	47.7	1.04	0.97	0.18	0.29	0.12						
C-16-106	47.16	1.07	1.01	0.23	0.25	0.10						
C-16-105	46.65	1.09	1.02	0.23	0.25	0.11						
C-16-103	45.57	1.07	0.99	0.23	0.36	0.13						
C-16-100	44.06	1.03	1.02	0.29	0.39	0.13						
C-16-98	42.92	1.04	0.99	0.23	0.34	0.12						
C-16-97	42.35	1.11	1.07	0.22	0.35	0.12						
C-16-96	41.82	1.10	1.05	0.24	0.34	0.13						
C-16-95	41.25	1.10	1.08	0.28	0.43	0.16						
C-16-93	40.16	1.08	1.05	0.22	0.31	0.12						
C-16-92	39.69	1.05	0.99	0.23	0.31	0.13						
C-16-90	38.66	1.10	1.09	0.27	0.35	0.14						
C-16-86	36.44	1.06	1.01	0.24	0.32	0.13						
C-16-85	35.94	1.07	1.04	0.23	0.34	0.14						
C-16-82	34.32	1.10	1.05	0.23	0.30	0.14						
C-16-81	33.8	1.08	1.02	0.16	0.32	0.14						
C-16-79	32.73	1.10	1.03	0.23	0.25	0.11						
C-16-77	31.67	1.08	1.03	0.25	0.28	0.13						
C-16-74	30.02	1.06	1.03	0.30	0.32	0.14						
C-16-71	28.43	1.05	1.00	0.20	0.28	0.14						
C-16-70	27.95	1.08	1.01	0.19	0.27	0.15						
C-16-67	26.25	1.08	1.01	0.25	0.29	0.14						
C-16-65	25.14	1.05	0.98	0.26	0.31	0.15	0.70	0.92	0.72	0.60	0.44	0.62
C-16-63	24.07	1.10	1.05	0.24	0.21	0.12						
C-16-61	23.07	1.10	1.05	0.25	0.33	0.13						
C-16-59	22.16	1.05	1.00	0.31	0.37	0.16						
C-16-58	21.68	1.04	1.01	0.32	0.37	0.16						
C-16-57	21.13	1.06	1.01	0.27	0.36	0.15						
C-16-54	19.66	1.06	0.99	0.23	0.32	0.12	0.58	1.03	0.69	0.54	0.46	0.61
C-16-53	19.14	1.05	1.04	0.24	0.27	0.11						
C-16-52	18.58	1.04	1.01	0.25	0.28	0.11						
C-16-50	17.58	1.05	1.00	0.26	0.32	0.12						
C-16-49	17.06	1.11	1.07	0.28	0.35	0.13						
C-16-47	16.08	1.09	1.04	0.30	0.35	0.13						
C-16-46	15.62	1.10	1.09	0.28	0.35	0.12						
C-16-45	15.14	1.07	1.07	0.29	0.39	0.13						
C-16-44	14.69	0.99	0.93	0.19	0.33	0.19						

Appendix 6D Carbon geochemistry values with their respective sample ID and stratigraphic position.

Sample ID	Height (m)	$\delta^{13}\text{C}$	TIC (CaCO ₃ %)	TOC (C wt%)	Sample ID	Height (m)	$\delta^{13}\text{C}$	TIC (CaCO ₃ %)	TOC (C wt%)
C-16-97	42.35	-23.68	74.42	0.91	C-16-151	85.04	-24.55	68.13	1.18
C-16-96	41.82	-23.63	72.82	0.78	C-16-150	84.43	-24.56	67.76	1.19
C-16-95	41.25	-23.69	68.62	1.01	C-16-149	83.89	-24.71	67	1.21
C-16-94	40.71	-23.68	75.4	0.74	C-16-148	83.08	-24.59	64.63	1.27
C-16-93	40.16	-23.59	73.72	0.58	C-16-147	82.17	-24.69	60.7	1.25
C-16-92	39.69	-23.71	71.37	1.00	C-16-146	81.31	-24.60	58	1.36
C-16-91	39.19	-23.54	68.67	1.00	C-16-145	80.64	-24.67	62.66	1.27
C-16-90	38.66	-23.58	66.58	1.20	C-16-144	79.55	-24.63	57.84	1.52
C-16-89	38.09	-23.52	64	1.20	C-16-143	79.03	-24.61	63.13	1.39
C-16-88	37.54	-23.51	62.81	1.27	C-16-142	78.56	-24.74	59.64	1.61
C-16-87	36.98	-23.71	69.23	1.31	C-16-141	77.63	-24.71	59.12	1.59
C-16-86	36.44	-23.74	67.51	1.33	C-16-140	76.78	-24.76	62.25	1.39
C-16-85	35.94	-23.88	64.48	1.32	C-16-139	75.93	-24.96	54.92	1.44
C-16-84	35.42	-23.85	69.30	1.18	C-16-138	75.22	-25.09	56.6	1.83
C-16-83	34.86	-23.80	70.17	1.24	C-16-137	74.6	-25.01	59.25	1.71
C-16-82	34.32	-23.80	69.73	1.41	C-16-136	73.33	-24.96	65	1.57
C-16-81	33.8	-23.94	72.78	1.18	C-16-135	72.03	-24.57	74.85	0.41
C-16-80	33.3	-24.02	73.50	0.97	C-16-134	71.03	-24.36	72.13	0.54
C-16-79	32.73	-23.82	81.34	0.88	C-16-133	69.56	-24.25	61.15	1.13
C-16-78	32.25	-23.98	73.78	1.06	C-16-132	68.3	-24.69	68	0.73
C-16-77	31.67	-24.28	72.85	1.15	C-16-131	67	-24.28	64.97	1.05
C-16-76	31.13	-24.06	72.58	1.19	C-16-130	65.87	-24.15	64.41	1.09
C-16-75	30.57	-24.21	72.34	1.21	C-16-129	64.8	-24.16	68.58	1.05
C-16-74	30.02	-23.90	62.57	1.44	C-16-128	63.67	-24.16	72.15	0.78
C-16-73	29.5	-24.27	72.40	1.22	C-16-127	62.62	-24.16	70.6	0.90
C-16-72	28.95	-24.41	72.10	1.23	C-16-126	61.51	-24.15	62.52	1.09
C-16-71	28.43	-24.19	72.60	1.03	C-16-125	60.34	-24.12	74.42	0.77
C-16-70	27.95	-24.20	73.80	1.05	C-16-124	59.27	-23.96	73.75	0.65
C-16-69	27.4	-24.22	72.53	1.08	C-16-123	58.15	-23.92	72.87	0.99
C-16-68	26.81	-24.54	72.85	1.12	C-16-122	56.95	-23.98	71.99	0.83
C-16-67	26.25	-24.07	68.28	1.44	C-16-121	55.8	-23.74	72.66	0.75
C-16-66	25.7	-24.09	61.90	1.58	C-16-120	54.7	-23.63	70.62	0.93
C-16-65	25.14	-24.31	63.42	1.72	C-16-119	54.18	-23.75	73.86	0.69
C-16-64	24.62	-23.87	67.10	1.63	C-16-118	53.68	-23.67	72.2	0.79
C-16-63	24.07	-23.69	67.05	1.49	C-16-117	53.12	-23.64	75.68	0.79
C-16-62	23.55	-24.00	73.73	1.13	C-16-116	52.58	-23.44	70.93	0.84
C-16-61	23.07	-23.78	74.01	0.97	C-16-115	52.06	-23.57	72.48	0.79
C-16-60	22.61	-24.21	67.24	1.00	C-16-114	51.52	-24.03	73.19	0.75
C-16-59	22.16	-23.62	64.92	1.24	C-16-113	51.01	-23.80	72.92	0.83
C-16-58	21.68	-23.76	67.45	1.12	C-16-112	50.46	-23.87	73.12	0.93
C-16-57	21.13	-23.97	67.95	1.33	C-16-111	49.85	-23.74	71.13	0.82
C-16-56	20.68	-23.87	69.22	1.20	C-16-110	49.33	-23.70	71.79	0.89
C-16-55	20.14	-23.95	81.46	0.75	C-16-109	48.86	-23.67	75.5	1.01
C-16-54	19.66	-24.04	78.74	0.73	C-16-108	48.27	-23.79	76.71	0.84
C-16-53	19.14	-23.99	77.36	0.92	C-16-107	47.7	-23.64	71.2	0.99
C-16-52	18.58	-23.90	77.99	0.80	C-16-106	47.16	-23.64	72.09	0.82
C-16-51	18.08	-23.77	74.03	0.99	C-16-105	46.65	-23.63	66.54	1.04
C-16-50	17.58	-23.72	71.08	1.14	C-16-104	46.12	-23.62	78.41	0.74
C-16-49	17.06	-23.64	68.22	1.00	C-16-103	45.57	-23.60	76.59	0.67
C-16-48	16.58	-23.65	66.85	1.15	C-16-102	45.04	-23.66	75.07	0.72
C-16-47	16.08	-23.71	68.11	1.24	C-16-101	44.56	-23.64	70.51	0.81
C-16-46	15.62	-23.82	72.25	1.05	C-16-100	44.06	-23.59	69.56	1.04
C-16-45	15.14	-23.92	73.79	1.11	C-16-99	43.51	-23.56	73.13	0.89
C-16-44	14.69	-24.41	77.03	0.87	C-16-98	42.92	-23.62	77.07	0.71
C-16-43	14.29	-24.10	76.25	0.88					

Appendix 6E Absolute values of major elements (Al, Si, Ti, Fe, P) and RSTEs (V, Ni, Co, Cr, Cu, Mo) in ppm = parts per million.

Sample ID	Height (m)	Al	Si	Ti	Fe	P	V	Ni	Co	Cr	Cu	Mo	U
C-16-151	85.04	16460	41500	787	7802	166	27.5	17.8	0.7	30.6	3.9	2.2	0.53
C-16-146	81.31	22508	56082	1021	8984	184	36.3	22.7	0.8	40.0	4.8	2.2	0.64
C-16-145	80.64	19782	47536	852	7979	113	30.3	16.9	0.5	33.8	3.5	1.6	0.64
C-16-144	79.55	21860	54947	997	9448	166	36.6	16.1	0.6	35.1	4.8	2.0	0.61
C-16-143	79.03	18451	46084	862	8034	158	30.8	14.2	0.5	30.3	4.0	1.6	0.69
C-16-142	78.56	20549	51602	958	8189	154	33.9	15.0	0.4	34.4	3.9	1.9	0.65
C-16-140	76.78	19189	49050	906	9117	159	32.9	16.1	0.8	33.4	4.4	1.9	0.68
C-16-138	75.22	26142	66473	1186	13523	218	48.2	35.5	1.1	46.5	6.9	2.9	1.11
C-16-137	74.6	19136	49493	871	9635	178	33.1	25.9	0.7	31.7	5.1	2.7	0.69
C-16-135	72.03	14209	37058	729	6274	109	22.3	10.2	0.2	23.8	3.3	0.7	0.43
C-16-133	69.56	22422	56519	988	10136	158	35.2	32.2	0.7	36.6	5.5	3.0	0.65
C-16-132	68.3	18239	46334	849	7922	190	28.3	19.6	0.5	30.5	4.1	2.5	0.59
C-16-130	65.87	18902	49407	826	8748	169	29.4	31.1	0.9	34.8	4.7	3.1	0.62
C-16-128	63.67	14079	36063	646	6435	122	21.4	14.1	0.4	24.0	3.0	2.1	0.55
C-16-126	61.51	20792	52847	902	9178	203	33.5	29.2	0.7	34.5	6.4	2.8	0.61
C-16-125	60.34	15189	38532	615	6075	121	22.9	18.4	0.6	25.7	3.3	2.4	0.57
C-16-124	59.27	14429	36747	656	6119	109	22.5	23.9	0.5	26.8	7.7	2.0	0.59
C-16-123	58.15	13893	36482	603	5855	133	22.0	21.4	0.7	24.9	3.7	2.3	0.44
C-16-121	55.8	14671	37277	632	6377	139	23.7	18.9	0.6	25.4	4.0	1.3	0.49
C-16-120	54.7	16351	41508	700	5994	123	26.1	21.4	0.7	28.1	3.5	1.5	0.64
C-16-119	54.18	14141	36102	590	5600	150	22.6	15.6	0.3	23.1	3.5	1.5	0.52
C-16-116	52.58	16731	39430	698	6123	139	25.1	18.6	0.3	25.6	4.0	0.9	0.80
C-16-114	51.52	14686	36403	619	5735	139	22.3	18.5	0.3	23.1	4.0	1.0	0.65
C-16-112	50.46	14549	35211	615	5623	106	21.8	25.5	0.3	25.8	4.0	1.1	0.55
C-16-111	49.85	16081	37063	619	6919	135	22.9	18.5	0.3	26.8	3.5	1.1	0.47
C-16-109	48.86	13272	30607	518	6548	103	18.8	17.3	0.3	23.0	3.2	0.9	0.49
C-16-108	48.27	13039	30169	508	5647	131	18.4	14.5	0.4	22.6	2.9	0.6	0.43
C-16-107	47.7	15931	38314	638	7359	146	23.4	24.4	0.6	27.5	4.1	1.2	0.53
C-16-106	47.16	16935	37211	652	6895	171	23.5	15.4	0.5	25.9	3.5	0.5	0.48
C-16-105	46.65	19570	44735	787	8258	166	28.3	21.1	0.7	31.2	4.1	0.9	0.53
C-16-103	45.57	13450	30563	527	5300	127	18.4	21.6	0.4	22.9	2.9	1.1	0.48
C-16-100	44.06	18926	40328	694	8229	161	26.6	23.0	0.7	29.1	4.3	0.9	0.48
C-16-98	42.92	13171	29728	498	5484	144	18.2	17.5	0.5	22.6	3.1	0.8	0.47
C-16-97	42.35	14210	33046	558	6029	161	20.3	20.7	0.4	24.7	3.6	1.1	0.44
C-16-96	41.82	16091	37083	647	7027	139	23.8	16.1	0.6	25.8	4.1	0.7	0.69
C-16-95	41.25	18783	43074	713	7504	167	28.1	21.9	0.5	29.8	4.3	0.9	0.46
C-16-93	40.16	16793	37133	630	6331	157	23.9	20.0	0.3	27.4	3.4	0.8	0.46
C-16-92	39.69	15283	35754	591	6901	186	22.9	24.8	0.5	27.3	4.1	0.8	0.50
C-16-90	38.66	19166	41766	772	8349	137	30.0	26.3	0.7	29.2	4.3	2.0	0.48
C-16-86	36.44	17638	40143	643	6591	168	26.4	15.2	0.3	27.1	5.0	0.4	0.40
C-16-85	35.94	19376	44407	704	8521	180	30.0	16.5	0.4	28.0	4.8	0.4	0.52
C-16-84	35.42	16657	39339	632	8135	218	30.2	17.7	0.5	26.3	5.6	0.3	0.50
C-16-82	34.32	15563	36301	543	7303	180	27.3	15.7	0.5	24.6	4.9	0.4	0.51
C-16-81	33.8	14826	34238	536	6617	188	24.4	14.0	0.5	22.7	4.1	0.4	0.51
C-16-79	32.73	9191	20902	338	4584	124	14.0	12.8	0.5	21.0	3.4	0.3	0.38
C-16-77	31.67	12971	30576	479	6691	179	21.0	21.4	0.5	24.0	4.9	0.5	0.58
C-16-74	30.02	19126	45477	735	10114	208	32.1	26.6	0.7	31.1	6.4	1.3	0.80
C-16-71	28.43	12857	30532	504	5663	159	20.8	18.6	0.4	22.6	4.0	0.4	0.51
C-16-70	27.95	12684	29438	486	5443	130	19.7	14.8	0.4	22.1	3.6	0.5	0.48
C-16-67	26.25	14351	32729	545	6727	177	22.3	22.0	0.7	24.3	4.5	1.0	0.56
C-16-65	25.14	16772	38806	662	9419	173	29.3	37.7	1.4	35.5	6.2	1.9	0.68
C-16-63	24.07	14221	33546	619	7703	170	22.8	30.1	1.0	29.8	4.8	1.6	0.52
C-16-61	23.07	14006	32507	590	6801	142	22.9	24.7	0.8	28.8	4.3	1.4	0.54
C-16-59	22.16	20322	47721	826	9702	234	32.5	24.3	0.8	34.7	5.1	1.2	0.60
C-16-58	21.68	18907	44518	739	9439	211	31.5	27.3	0.9	35.5	5.3	1.4	0.64
C-16-57	21.13	17973	41011	736	8194	173	30.3	31.6	1.4	35.8	5.5	1.5	0.57
C-16-54	19.66	11898	26783	459	4947	162	18.8	18.4	0.5	24.4	3.6	0.8	0.43
C-16-53	19.14	12163	27035	470	5708	167	19.7	18.2	0.6	23.0	4.0	0.9	0.44
C-16-52	18.58	11948	27752	474	6088	139	20.2	17.5	0.6	22.8	3.6	0.9	0.46
C-16-50	17.58	15016	34224	620	7722	148	26.4	27.4	0.8	29.4	4.6	1.1	0.55
C-16-49	17.06	17747	40515	722	9299	170	30.8	21.1	1.0	33.3	5.6	0.9	0.64
C-16-47	16.08	17088	39108	688	8287	192	30.2	20.0	0.7	29.6	4.4	0.8	0.49
C-16-46	15.62	15001	32890	594	7700	242	26.8	31.0	1.2	29.6	4.9	0.9	0.54
C-16-45	15.14	13986	30516	551	7182	159	25.7	27.4	1.1	27.6	4.6	1.5	0.47
C-16-44	14.69	12152	27058	472	6333	198	22.5	21.7	0.9	24.3	4.2	1.2	0.49
Average %RSD		5.1	2.3	4.5	8.3	5.1	2.5	9.4	30	6.1	14	9.9	6.5

7 DEMISE OF OM-RICH FACIES AND CHANGING PALEOENVIRONMENTAL CONDITIONS ASSOCIATED WITH THE END OF CARBON ISOTOPE SEGMENT C5 OF OAE1A IN THE NORTH AND NORTHEASTERN IBERIAN PENINSULA

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Abstract

During the Cretaceous the concurrence of changing paleoceanographic and paleoclimatic conditions coupled with considerable variations in eustatic sea level contributed to brief episodes characterized by globally widespread deposition of organic matter (OM)-rich marine sediments collectively termed Oceanic Anoxic Events (OAEs). Here, the aim is to investigate the response of a lower Aptian hemipelagic sequence from the northeastern Iberian margin in the context of OAE1a and integrate the recorded signals within a broader spatial frame to establish parallelisms that may help in assessing the regional expression superimposed on the global factors related to this event.

Results from molecular thermal maturity indices with average ratios consistently below equilibrium values indicate thermal immaturity, with minor to no effect on the organic geochemical signals. Source-specific biomarkers demonstrate that the OM consists of a mixture of autochthonous marine and allochthonous terrigenous sources, typical of hemipelagic settings. Stable carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) data are consistent with the pattern reported for the end of carbon isotope segment C5 within OAE1a. Moreover, high sediment accumulation rates (bulk = 37.13 cm/kyr, wet = 63.29 cm/kyr) for this interval, permits to establish refined details suitable for precise chemostratigraphic correlations. Integration of field observations, microfacies and geochemical data allows

the recognition of three distinct Units. Within Unit 1, variable pulses of fluvial fluxes associated with climate fluctuations explain the alternating lithology with limestones depicting the least terrestrially influenced endmember and marlstones representing episodes of highest terrigenous input. Primary production enhanced during periods of intensified fluvial inputs of biolimiting elements (P, Fe) provided abundant labile OM conducive to oxygen-deprived conditions as attested by concomitant peaks in total organic carbon (TOC), relatively lower benthic faunal counts, lower bioturbation index, higher concentration of pyrite and enrichments in redox sensitive trace elements (RSTEs). In the ensuing marlstone-dominated Unit 2-interval, results show relatively higher TOC, RSTEs, P, Fe, Al, Si, and Ti values than before. These results suggest that an increase in runoff due to established humid continental conditions prevailed in this period with quasi-permanent eutrophic surface waters and continuously established oxygen-deprived conditions, but still without a fully anoxic phase, as benthic fauna while relatively reduced are still present throughout. At the same time, higher gammacerane index in this interval attests to a stratified water column, which may have been a controlling factor in preventing vertical mixing and oxygenation of the basin. Unit 3 registers a sharp change with hard limestones impoverished in TOC, Al, Si, Ti, P and Fe, and with lower relative proportion of autochthonous to allochthonous OM, indicating a reduction in fluvial fluxes and surface water fertility linked to dryer climate conditions, as further suggested by an increase in smectite and a decrease in illite content. In accord, RSTEs decrease and gammacerane indices drop to near zero, signaling the termination of density stratification and renewed ventilation of the water column. Simultaneous changes in microfacies, with coarser grained packstones, with reduced planktonic foraminifera

and an increase in benthic taxa, imply a shallowing of the basin, similar to that reported for sequences in the neighboring Basque-Cantabrian Basin synchronous with the negative $\delta^{13}\text{C}_{\text{org}}$ shift heralding the end of carbon isotope segment C5.

7.1 Introduction

The sedimentary expression of marine depositional sequences are primarily controlled by the interactions between global forcing variables, including eustatic sea level and climatic fluctuations, plate tectonics, astronomical cycles, and to local variables such as regional tectonics, sediment supply, basin physiography, atmospheric and basinal circulation patterns, and biotic community structure and dynamics (Posamentier et al., 1988; Haq, 1995; Brenchley and Harper, 1998; Flügel, 2004; Tucker and Wright, 2009; Pomar and Kendall, 2012). The Early Aptian witnessed pronounced changes in the ocean/climate system, and as such had a remarkable impact on the associated sedimentary record (Jenkyns, 2003; Föllmi, 2012). Potential causes of these changes include the restructuring of both, major landmasses and ocean/atmosphere circulation patterns and extreme greenhouse conditions, likely triggered by the outgassing of CO_2 during the emplacement of large igneous provinces (LIPs e.g. Ontong Java-Manihiki-Hikurangi plateau) combined with coeval intervals of intensified oceanic crust production (Arthur et al., 1985; Barron and Washington, 1985; Larson, 1991; Tarduno et al., 1991; Larson and Erba, 1999; Leckie et al., 2002; Erba and Tremolada, 2004; Weissert and Erba, 2004; Méhay et al., 2009; Tejada et al., 2009; Van Der Meer et al., 2014; Wang et al., 2014; Sun et al 2016; Naafs et al., 2016; Charbonnier and Föllmi, 2017). Additionally, the presence of extensive wetlands may have provided water vapor as a supplementary greenhouse gas (Hay et al., 2019).

In response to globally warm climates, reduced equatorial to polar temperature gradients probably developed, thus decreasing the ocean-heat transport system (Barron, 1983; Huber et al., 1995; 2018; Littler et al., 2011; Jenkyns et al., 2012; Mutterlose et al., 2014; O'Brien et al., 2017). Concurrent increases in continental weathering and runoff induced by intensified hydrological cycles may have occurred (Barron et al., 1989; Blättler et al., 2011; Föllmi, 2012; Lechler, 2015; Charbonnier et al., 2018).

Superimposed or interlaced are also long and short-term eustatic sea level rises, which formed large epicontinental seas (Haq, 2014). The concurrence of changing paleoceanographic and paleoclimatic conditions, and considerable variations in sea level deeply affected the depositional pattern of most marine settings at that time (Föllmi et al., 1994; Burla et al., 2008; Huck et al., 2010; Föllmi, 2012). For instance, carbonate platforms in the Tethyan realm witnessed a complete shutdown (Funk et al., 1993, Föllmi et al., 1994; Weissert et al., 1998; Bosellini et al., 1999; Graziano, 1999; Wissler et al., 2003; Föllmi and Gainon, 2008; Gaona-Narvaez et al., 2013; Godet, 2013; Pictet et al., 2015) and a micro-encrusting-dominated community temporarily replaced once flourishing rudist and coral reefs, especially along the southern Tethyan margin (Immenhauser et al., 2005; Huck et al., 2010; Rameil et al., 2010). Equally, deeper hemipelagic and pelagic settings of the Tethys and elsewhere were affected, recording black shales with high OM content (Bralower et al., 1994; Cobianchi et al., 1999; Dumitrescu and Brassell, 2005; Dumitrescu et al., 2006; de Gea et al., 2008; Heldt et al., 2008; Emeis and Weissert, 2009; Patruno et al., 2015). This interval, estimated to have lasted ~ 1.1 Ma (Li et al., 2008; Malinverno et al., 2010) in the Early Aptian is recognized as Oceanic Anoxic Event 1a (OAE1a), because most sequences show

Figure 7-1 A) Location map of the Organyà Basin in the Iberian Peninsula. B) Regional geologic map showing the area of interest. A) and B) Modified from Dinarès-Turell and García-Senz, 2000). C) Detailed geologic map of the studied area showing the location of the El Pui Section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) and the El Pujal Section (Socorro and Maurrasse, 2019a,b); and this study). C) Modified from Gong et al. (2009). D) Satellite image showing the portion of the El Pujal Section studied thus far (Basal Portion - Socorro and Maurrasse, 2019a; Middle Portion - Socorro and Maurrasse, 2019b; Uppermost Portion - This study). D) Modified from Google Earth Map Data 2018. E). Photograph of the uppermost portion of the outcrop showing remarkably hard, closely spaced grayish orange (10 YR 7/4) beds, intercalated by medium light gray (N6) beds, with an enduring hard nature. F) Photograph of a portion of the outcrop showing a large expanse of dark gray to medium dark gray (N3 to N4), marly beds.

7.2 Geologic Setting

The Late Jurassic to Early Cretaceous initiation of strike-slip movement of Iberia relative to Europe associated with the plate tectonic kinematic evolution of the Bay of Biscay and the North Atlantic generated a series of depocenters, including the Basque-Cantabrian Basin, the North Pyrenean Basin and the Central Pyrenean Basin. (Masson and Miles, 1984; Puigdefàbregas and Souquet, 1986; Berástegui et al., 1990; Vergés and García-Senz., 2001; García-Senz., 2002; Rosenbaum et al., 2002; Sibuet et al., 2004; Gong et al., 2008; 2009; Jammes et al., 2010; Vissers and Meijer., 2012). The Organyà Basin forms part of the Central Pyrenean Basin and thus represents one such example of these extensional basins (Berástegui et al., 1990; García-Senz 2002). Associated sedimentary deposits archive expansive (~ 4 km-thick) sequences consisting of shallow, platform carbonates and hemipelagic to pelagic marine sediments that span the upper Tithonian to the lower Turonian (Berástegui et al., 1990; García-Senz, 2002). During the Early and mid-Cretaceous, the Organyà Basin was located along an elongated, narrow stretch of sea (~ 200 km) that extended from the proto-North Atlantic to the southeast, cutting between Iberia and Europe (Jammes et al., 2009; Vacherat et al., 2017). Eventual northward movement of Africa and collision of Iberia with Europe associated with the Late Cretaceous to Cenozoic Pyrenean Orogeny brought about the closure and inversion of these Mesozoic sedimentary basins (Vergés and García-Senz., 2001; García-Senz 2002; Golonka, 2004).

In its present position, the Organyà Basin is located in the South-Central Pyrenees of Spain on the eastern portion of the South Pyrenean Central Unit (SPCU). Rocks associated with the Basin largely outcrop in the hanging wall of the Bóixols thrust sheet,

bound to the north by the Morreres backthrust (Gong et al., 2008; 2009; Mencos et al., 2015). As illustrated by García-Senz (2002), the internal geometry of its remnants is structurally dominated by the east to west trending asymmetric Santa Fé syncline (Fig. 7-1C). Samples for this study were collected from the northern limb of the syncline, south of the Cabó River Valley (Fig. 7-1C). The section is well exposed and easily accessible via the Avenida Santa Fé road, which stems from the main town of Organyà. Here, we focus on the uppermost 85.82 m-interval or third segment of the composite El Pujal section which includes two previously studied segments: the basal 13.77 m (Socorro and Maurrasse, 2019a) and the middle 70.75 m-interval (Socorro and Maurrasse, 2019b), continuous with the neighboring El Pui section (Fig. 7-1C) (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016).

7.3 Experimental Methods

7.3.1 Sampling and Microscopic Analysis

The 106 samples of this interval were collected from well-exposed outcrops near the hamlet of El Pujal de Cabó in the municipality of Organyà. They achieved an approximate resolution of one sample every 0.81 cm over a distance of 85.82 m (86.07 m – 171.89 m), representative of the uppermost portion of the El Pujal Section (42°13'04.8"N 1°18'35.3"E) (Fig. 7-1D, E, F). The preparation and petrographic study of thin sections (n = 106) were performed at Florida International University (FIU). Microfacies analysis was accomplished on an Olympus BH-2 petrographic microscope. To complement field observations, the microscopic study also considered content and quantity of the benthic fauna, and degree of bioturbation which was assigned a value ranging from 0 to 6 following the description in Taylor and Goldring (1993). Counts of

benthic foraminifera and echinoid fragments were taken from thin sections and are thus expressed as number of specimens per cm² or ρ. Compositional proportions were assessed using visual estimates as summarized by Terry and Chilingarian (1955). Color description of samples at all scales is based on the modified Munsell color system as proposed by Goddard et al. (1963). Petrographic classification of carbonate rocks described here follows the guidelines of Folk (1959) and (1962). Index planktonic foraminifera were identified with the aid of illustrations in published works by Verga and Premoli-Silva (2002), Heldt et al. (2008) and Moullade et al. (2015). In addition, certain samples (limestone intervals n = 17) were selected to be counted for the ratio between planktonic and benthic foraminifera as a tool to estimate paleodepths. The ratio is expressed as the percentage of planktonic foraminifera or %P and depth is calculated using the relationship between bathymetry and %P as proposed by van der Zwaan et al. (1990):

$$\text{Depth (m)} = e^{(3.58718 + (0.03534 * \%P))}$$

The %P is the percentage planktonics in the total foraminiferal association, calculated as $100 * P / (P + B)$, where P is the number of planktonic individuals and B is the number of benthic individuals.

7.3.2 Bulk Carbon Geochemistry

Organic carbon (TOC) and carbonate (TIC) contents were measured from 106 powdered rock samples at FIU within the Carbon Analysis Laboratory (CAL) using a LECO CR-412 carbon analyzer following the methodology detailed in Socorro and Maurrasse (2019a) and references therein. The instrument was calibrated by creating a 15-point linear calibration curve using C64-500 Fisher Scientific $\geq 99.0\%$ calcite

standard and the accuracy (0.15%) of the calibration was verified by analyzing a dolomitic limestone standard (NIST 88b). The analytical precision calculated from the coefficient of variation of four replicate runs ($\bar{x} = 76.66\%$ $s = 0.07\%$) of the same sample was 0.09%. Results of the TOC/TIC analyses are reported as percentages of total dry weight of organic carbon (C wt%) and inorganic carbon (CaCO_3 %), respectively in the bulk sample. TIC values are used to assign a general lithologic nomenclature modified from Sanchez-Hernandez and Maurrasse (2014) to enable for better representation of lithologic variation observed in the field, whereby $\text{TIC} > 70\% = \text{limestone}$, $65\% - 70\% = \text{argillaceous limestone}$, and $35\% - 65\% = \text{marlstone}$.

Stable carbon isotope analysis was conducted at the FIU Stable Isotope Laboratory (SIL) on the bulk organic ($\delta^{13}\text{C}_{\text{org}}$) fraction of 106 powdered samples. Prior to the analysis, samples were processed following the procedures outlined in Socorro and Maurrasse (2019a) and references therein. The $\delta^{13}\text{C}_{\text{org}}$ values were measured using a Thermo Scientific Delta V elemental analyzer isotope ratio mass spectrometer (EA-IRMS) and the results are expressed as per mil (‰) relative to the Vienna-Pee Dee Belemnite (VPDB) standard. The analytical precision calculated from the standard deviation of 32 replicate glycine standard samples was better than 0.58‰.

7.3.3 Elemental Concentration Analysis

Concentrations of major elements including silicon (Si), aluminum (Al), titanium (Ti), phosphorus (P), iron (Fe) and redox-sensitive trace elements (RSTEs) including vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), molybdenum (Mo) and uranium (U) were analyzed from 37 samples distributed throughout the studied interval and selected to be representative of lithologic variations. Sample preparation

followed the general method developed for the routine analysis of soils and sediments by Arroyo et al. (2009), and further detailed in Sanchez-Hernandez and Maurrasse (2014) and Socorro and Maurrasse (2019a). Analyses were conducted at the FIU Trace Evidence Analysis Facility (TEAF) using an ELAN DRC II (Perkin Elmer LAS) inductively coupled plasma mass spectrometer (ICP/MS). Samples were introduced via laser ablation using an Applied Spectra J200 266 nm Nd–YAG laser set at a spot size of 200µm and a frequency of 10Hz. Prepared pellets were ablated 5 times and the results were averaged for each sample. Integration of raw data was performed on the GLITTER software. Analytical precision calculated from the coefficient of variation averaged 2.1% (Si), 1.7% (Al), 5.4% (Ti), 12% (Fe), 9.4% (P), 5.7% (V), 12% (Ni), 14% (Co), 15% (Cr), 18% (Cu), 12% (Mo) and 17% (U). Analytical performance of the method was evaluated by running 3 standard reference materials (NIST2710, PACS-2, NIST2704) at the start, every 10 samples, and at the end of the analysis. Results for major elements are expressed as parts per thousand ($\text{ppm} \cdot 10^{-3}$) and RSTEs are expressed as parts per million (ppm).

Following early works by Turekian and Wedepohl (1961), and Wedepohl, (1971) enrichments in RSTEs relative to the background natural value denote sediments deposited under reducing conditions (e.g., Brumsack, 1980, 2006; Calvert and Pedersen, 1993; Dean, 1999; Yarincik., et al., 2000; Tribovillard et al., 2004, 2006; Pattan and Pearce, 2009; Föllmi et al., 2012; Stein et al., 2012; Westermann et al., 2013; Ruebsam et al., 2017). The uncertainty about the actual magnitude of the background natural value or detrital signal, unrelated to the redox conditions at the time of deposition, is undoubtedly the pitfall of this method (Van Der Weijden, 2002; Cole et al., 2017; Socorro and

Maurrasse 2019b). Therefore, we rely on a baseline detrital value, previously calculated for the region by Socorro and Maurrasse (2019b) and referred to as the Organyà Basin's Average Background Value (OBABV), to assess enrichment indices (EIs) relative to the natural background levels.

$$EIs = \frac{[RSTEs]}{[RSTEs]_{\text{regional background}}}$$

In this equation [RSTEs] is the concentration in ppm of a particular element in a sample and $[RSTEs]_{\text{regional background}}$ is the average value in ppm of the corresponding RSTE from the calculated OBABV of Socorro and Maurrasse (2019b). OBABV averages of V, Cr, Co, Ni, Cu, Mo and U are 27.56 ppm, 33.46 ppm, 3.68 ppm, 32.31 ppm, 5.72 ppm, 2.56 ppm, and 1.10 ppm, respectively. Relative enrichments are thus expressed as $EIs > 1$, whereas depleted elemental values are represented by $EIs < 1$. To allow for easier correlation between RSTEs and other proxies, we calculated $\sum EIs$ by adding all the EIs of each element for each sample.

7.3.4 Lipid Extraction and Analyses

Powdered samples ($n = 26$) were processed and analyzed following the methodology outlined in Socorro and Maurrasse (2019a) and references therein. The analysis focused on the distribution of the aliphatic fraction; hence, total lipid extracts (TLE) were separated from the aromatic and polar fraction by elution with 4 ml of hexane using a silica gel-packed glass pipette. The collected fractions were concentrated down to 1 ml and stored at 4°C in amber vials before analysis.

Aliphatic fractions ($n = 26$) were analyzed at the FIU Advanced Mass Spectrometry Facility via gas chromatography-mass spectrometry (GC/MS) technique using an Agilent

6890/Agilent 5973 GC/MS. A 5 μ L volume of each sample was injected in split-less mode through an HP-5MS UI 30 m, 0.25 mm, 0.25 μ m, capillary column. The injector temperature was set at 280°C and the oven temperature program was set to hold at 65°C for 2 min, then ramped to 300°C at a rate of 4°C/min and held at 300°C for 8 min. The single quadrupole MS detector was configured in scan mode to monitor from 42 to 500 m/z. The resulting data was analyzed using OpenChrom.

Selected aliphatic fractions (n = 10) were further analyzed for their distribution of hopanes and steranes at the FIU Advanced Mass Spectrometry Facility using a Bruker EvoQ GC triple quadrupole (TQ) MS in metastable reaction monitoring (MRM) mode (MRM-GC-MS/MS). A 1 μ L volume of each sample was injected in split-less mode through an HP-5MS 60 m, 0.25 mm, 0.25 μ m, capillary column. The injector temperature was set at 260°C and the oven was programmed from 65°C for 2 min, followed by a temperate ramp of 4°C/min up to 310°C and held isothermally for 10 min. Metastable transitions of C₂₇, C₂₈, C₂₉, C₃₀, C₃₁, C₃₂, C₃₃, C₃₄ and C₃₅ hopanes included m/z: 370 $\rightarrow$ 191 (370.40 $\rightarrow$ 191), 384 $\rightarrow$ 191 (384.40 $\rightarrow$ 191), 398 $\rightarrow$ 191 (398.4 $\rightarrow$ 191), 412 $\rightarrow$ 191 (412.40 $\rightarrow$ 191), 426 $\rightarrow$ 191 (426.40 $\rightarrow$ 191), 440 $\rightarrow$ 191 (440.40 $\rightarrow$ 191), 454 $\rightarrow$ 191 (454.50 $\rightarrow$ 191), 468 $\rightarrow$ 191 (468.50 $\rightarrow$ 191), and 482 $\rightarrow$ 191 (482.50 $\rightarrow$ 191), respectively. Metastable transition of C₂₇, C₂₈, C₂₉, C₃₀ steranes included m/z: 372 $\rightarrow$ 217 (372.40 $\rightarrow$ 217), 386 $\rightarrow$ 217 (386.40 $\rightarrow$ 217), 400 $\rightarrow$ 217 (400.40 $\rightarrow$ 217), and 414 $\rightarrow$ 217 (414.40 $\rightarrow$ 217), respectively. The compounds were identified by comparing retention times and elution patterns with GC-MS/MS results from literature references (Peters et al., 2005; Peters et al., 2007; Ahmed et al 2013).

The terrigenous to aquatic ratio (TAR) was determined using the equation proposed by Bourbonniere and Meyers (1996):

$$\text{TAR} = \frac{n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31}}{n\text{C}_{15} + n\text{C}_{17} + n\text{C}_{19}}$$

The relative abundance of odd to even preferences of long-chain length *n*-alkanes were determined using the carbon preference index (CPI) after Bray and Evans (1961):

$$\text{CPI} = \frac{1}{2} \left[\frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{24} + n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32}} + \frac{n\text{C}_{25} + n\text{C}_{27} + n\text{C}_{29} + n\text{C}_{31} + n\text{C}_{33}}{n\text{C}_{26} + n\text{C}_{28} + n\text{C}_{30} + n\text{C}_{32} + n\text{C}_{34}} \right]$$

Various hopane and sterane parameters were calculated as follows:

$$\frac{\text{Ts}}{\text{Ts} + \text{Tm}} = \frac{18\alpha \text{ 22,29,30 trisnorhopane}}{18\alpha \text{ 22,29,30 trisnorhopane} + 17\alpha \text{ 22,29,30 trisnorhopane}}$$

$$\text{C}_{31} \frac{22\text{S}}{22\text{S} + 22\text{R}} = \frac{\text{C}_{31} \text{ 17}\alpha, 21\beta(\text{H}) \text{ homohopane (22S)}}{\text{C}_{31} \text{ 17}\alpha, 21\beta(\text{H}) \text{ homohopane (22S)} + \text{C}_{31} \text{ 17}\alpha, 21\beta(\text{H}) \text{ homohopane (22R)}}$$

$$\text{Gammacerane Index} = \frac{\text{C}_{30} \text{ Gammacerane}}{\text{C}_{30} \text{ 17}\alpha, 21\beta(\text{H}) \text{ hopane}}$$

$$\% \text{C}_{27} \alpha \alpha \alpha \text{R} = \frac{100 * \text{C}_{27} \text{ 5}\alpha, 14\alpha, 17\alpha(\text{H}) \text{ sterane (20R)}}{\text{C}_{27} + \text{C}_{28} + \text{C}_{29} \text{ 5}\alpha, 14\alpha, 17\alpha(\text{H}) \text{ sterane (20R)}}$$

$$\% \text{C}_{28} \alpha \alpha \alpha \text{R} = \frac{100 * \text{C}_{28} \text{ 5}\alpha, 14\alpha, 17\alpha(\text{H}) \text{ sterane (20R)}}{\text{C}_{27} + \text{C}_{28} + \text{C}_{29} \text{ 5}\alpha, 14\alpha, 17\alpha(\text{H}) \text{ sterane (20R)}}$$

$$\%C_{29}\alpha\alpha\alpha R = \frac{100 * C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20R)}}{C_{27} + C_{28} + C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20R)}}$$

$$\frac{C_{27}}{C_{29}} = \frac{C_{27} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20R)}}{C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20R)}}$$

$$C_{29} \frac{20S}{20S + 20R} = \frac{C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20S)}}{C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20S)} + C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20R)}}$$

$$C_{29} \frac{\beta\beta}{\beta\beta + \alpha\alpha} = \frac{C_{29} 5\alpha, 14\beta, 17\beta(H) \text{ sterane (20S + 20R)}}{C_{29} 5\alpha, 14\beta, 17\beta(H) \text{ sterane (20S + 20R)} + C_{29} 5\alpha, 14\alpha, 17\alpha(H) \text{ sterane (20S + 20R)}}$$

7.3.5 Bulk and Clay Mineral Analyses

Bulk and clay mineral (< 2 µm fraction) analyses were performed on selected samples (n = 10) via X-ray diffraction (XRD) method at the Illinois State Geological Survey in the Prairie Research Institute of the University of Illinois. For the analysis of bulk-mineral content, samples were micronized with deionized (DI) water for 10 min in a McCrone micronizing mill. To remove the majority of the DI water, the samples were transferred to 50 mL tubes and centrifuged for 20 min at 2000 rpm, after which the clear supernatant was poured off. The remaining sample was dried overnight at 40°C, homogenized with a mortar and pestle and packed into an end-loading sample holder as a random powder bulk-pack. The prepared samples were analyzed on a Scintag XDS2000 diffractometer with data collection set from 2° to 60° 2θ with a fixed time of 5 seconds per 0.05° 2θ for each sample. The intensity of the identified mineral phases, including quartz, potassium feldspar (K-feldspar), plagioclase feldspar (P-feldspar), calcite,

dolomite, siderite, pyrite/marcasite and bulk clay, was analyzed using the semi-quantitative data reduction software Jade+ and reported as relative percent.

The composition of the clay mineral fraction ($< 2 \mu\text{m}$) was determined using oriented and glycolated clay slides following the procedure detailed in Socorro and Maurrasse (2019b). The slides were analyzed with a Scintag XDS2000 diffractometer set to collect data from 2° to $34^\circ 2\theta$ at a fixed rate of 2° per minute and a step size of $0.05^\circ 2\theta$. Smectite, illite, kaolinite and chlorite were identified and their proportions, expressed as relative percent, were acquired using the Jade+ software.

7.3.6 Correlation Analysis

Correlation coefficients were determined for various proxies using Microsoft Office Excel 2013. The correlation coefficient is based on the Pearson's r equation expressed as:

$$\text{Correl (X,Y)} = \frac{\sum(x - \bar{x})(y - \bar{y})}{\sqrt{\sum(x - \bar{x})^2 \sum(y - \bar{y})^2}}$$

Where $\bar{x}$ and $\bar{y}$ are the corresponding sample's average. The results of this equation go from a perfect negative correlation (-1), no correlation (0) to a perfect positive correlation (1). Values in between will be labeled as 0.1-0.3 = weak, 0.4-0.6 = moderate, 0.7-0.9 = strong.

7.4 Results

7.4.1 Field Observations and Petrographic Analysis

Field observations of the uppermost 85.82 m portion of the El Pujal section reveals a sequence that generally consists of marlstone and limestone beds (Fig. 7-2A) with superficially medium light gray (N6) to dark gray (N3) coloration and a flaky appearance (Fig. 7-2B) that dissipates at depth as the unweathered rocks are well lithified. The

lithostratigraphic pattern recorded in this interval permits the recognition of three distinct units. Unit 1 spans from 86.07 m up to ~ 114.15 m (~ 28 m) and is composed of a repetitive series of differentially weathered packets of indurated beds that are followed by soft, easily weathered, argillaceous to marly beds (Fig. 7-2A, B). This pattern transitions into Unit 2, which spans from 114.15 m to ~ 167.96 m (~ 53.81 m) and consists of dark gray to medium dark gray (N3 to N4), marly beds, interspersed with at least three intervals of protruding, indurated beds (Fig. 7-2A, B). Unit 3 extends from 167.96 m up to 171.89 m (~ 3.93 m) and constitutes a distinct facies change, as it is dominated by remarkably hard, closely spaced grayish orange (10 YR 7/4) beds, intercalated by medium light gray (N6) beds (Fig. 7-2A, B).

The microscopic analysis reveals temporal changes in allochems, texture and fabric of the matrix, in accord with field observations. A uniform, kerogen rich, micritic matrix with less than 30% allochems including dispersed pyritized skeletal fragments characterizes Unit 1 (Fig. 7-2C), which reveal subtle differences in benthic faunal content and degree of bioturbation between the different lithology. The indurated beds contain higher benthic foraminifera ρ , echinoid fragment ρ and a higher degree of bioturbation (≥ 5) as compared with the softer, argillaceous to marly beds (Fig. 7-3A, B, C). Moreover, relative to the more indurated beds, marly intervals contain higher abundances of pyrite, which is found disseminated throughout as euhedral crystals and infilling bioclasts. Skeletal remains consist mainly of planktonic and benthic foraminifera, echinoderm fragments, sponge spicules and minute gastropods (300 - 800 μm).

Figure 7-2 A) Simplified lithostratigraphic column depicting the distribution of various lithologies present in this studied interval. Units 1-3 refer to various lithostratigraphic units demarcated based on their respective lithological pattern. B) Outcrop photographs representative of each Unit, scale at 2 m. C). Thin section images representative of each Unit, scale at 200 μm .

Unit 2 is dominated by biomicrites (Fig. 7-2C) with a relatively lower degree of bioturbation (generally < 4), impoverished benthic fauna ρ and less than 10% allochems (Fig. 7-3A, B, C), most of which are completely infilled with pyrite (Fig. 7-2C). The composition of bioclasts in Unit 2 is identical to Unit 1, except that nearing the top, at ~ 150.21 m, the monotonous microfacies is interrupted by a gradual increase of calcareous sponge spicules. Additionally, a subtle coarsening of the grains recognized at ~ 162.39 m precedes the uppermost portion of Unit 2 starting at 167.61 m, where microfacies transition into mainly packed biomicrites. Unit 3 is marked by further grain coarsening and a microfacies shift towards highly bioturbated (>5), packed biosparites (Fig. 7-2C).

Figure 7-3 A) and B) Time series counts of benthic foraminifera and echinoid fragments. C) Bioturbation index for each sample following the proposed scheme in Taylor and Goldring (1993). A-C) Bluish bands correspond to argillaceous limestone and marlstone intervals. D) Limestone interval counts of the ratio between planktonic and benthic foraminifera. The ratio is expressed as the percentage of planktonic foraminifera or %P calculated as $100 \cdot P / (P+B)$, where P is the number of planktonic individuals and B is the number of benthic individuals. E) Calculated paleodepths based on the relationship between bathymetry and %P as proposed by van der Zwaan et al. (1990). Solid red lines represent the average depth value.

These rocks contain on average >50% allochems dominated by a fibrous matrix of sponge spicules, abundant and diversified benthic foraminifera assemblages, in particular *Glomospira* sp. (Fig. 7-2C), increased echinoid skeletal debris, but lesser amounts of planktonic foraminifera as compared to previous Units 1 and 2 (Fig. 7-3A, B, C, D).

The Zonal marker *Leupoldina cabri* (*L.cabri*), originally identified in the basal portion (height of 13.77 m) of the El Pujal sequence (Socorro and Maurrasse, 2019a), ubiquitous henceforth (Socorro and Maurrasse, 2019b), also occurs at 28 intervals of Unit 1, and 2, but disappears in Unit 3 (Fig. 7-3 marked with an X next to lithologic column). Further analysis of planktonic foraminifera focusing on their percentages (%P) in limestone intervals (n = 17), yielded an average %P of 79% for the lower Unit 1 and 18% for uppermost Unit 3 (Fig. 7-3D). Utilizing the relationship of %P and depth (van der Zwaan et al., 1990), these values suggest an estimated average depth of 613 m for Unit 1 and 70 m for Unit 3 (Fig. 7-3E), a decrease of 543 m.

7.4.2 Inorganic, Organic and Carbon Isotope Stratigraphy (TIC, TOC and $\delta^{13}\text{C}_{\text{org}}$)

The carbonate content (TIC) throughout this 85.82 m interval varies from 54.31% to 85.63% with an average of 64.59% (Fig. 7-4A) (For a complete list of values refer to Appendix 7A). The differentially weathered packets of alternating marlstones and limestones that comprise Unit 1 (86.07 m -114.15 m) show considerable fluctuation in TIC values (56.67 % to 73.15%). The overlying Unit 2, consisting mostly of marlstones, shows a distinct decline in TIC, with an average of 61.91%. This pattern continues up to the very top of Unit 2, after which values gradually increase as the lithology transitions into a limestone dominated, 3.93 m interval (Unit 3), where carbonate content averages 79.17% and peaks up to 85.63%.

The organic carbon content (TOC) of the studied samples averages 0.90% and varies from 0.27% to 1.29% (Fig. 7-4B) (For a complete list of values refer to Appendix 7A). Overall, a clear inverse relationship between TOC and TIC ($r = -0.77$) is visible with enriched TOC values in argillaceous limestone and marlstone beds. Samples in the lower 28.08 m of Unit 1 contain on average 0.78% organic carbon, with pronounced peaks up to 1.07%, 1.24% and 0.90% at 89.51 m, 100.1 m and 108.19 m, respectively. Unit 2 shows a sharp increase in TOC ($\bar{x} = 1.01\%$), with values generally above the section's

average up to ~ 152 m. Subsequently, TOC values fluctuate between 1.18% and 0.54% up to a stratigraphic height of 166.81 m, and then gradually gradually decrease to 0.46% at 167.96 m, which marks the transition into the succeeding Unit 3. The TOC values decline in Unit 3 ($\bar{x}$ = 0.47%) reaching a minimum of 0.27% at 168.36 m, the lowest recorded value of the entire El Pujal sequence.

The stable carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) measured in the bulk organic fraction averages -24.26‰ with values that vary between -25.31‰ and -23.91‰ (Fig. 7-4C) (For a complete list of values refer to Appendix 7A). Overall, the $\delta^{13}\text{C}_{\text{org}}$ curve displays a weak negative relationship with TIC (r = -0.36) and a weak positive relationship with TOC (r = 0.28). The lowermost part of the section, equivalent to Unit 1, shows fluctuating values between -24.87‰ and -24.10‰. Overlying Unit 2 displays a uniform trend ($\bar{x}$ = -24.14‰) with only minor variability of ≤ 0.46 ‰. The most striking aspect of the $\delta^{13}\text{C}_{\text{org}}$ curve is a pronounced negative shift of 1.34‰, recorded in the uppermost 3.93 m of the succession or Unit 3 (Fig. 7-4C).

7.4.3 Distribution Pattern of Major and Trace Elements

Concentrations of major elements (Si, Al, Ti, P, and Fe) are presented in Figure 7-5 (For a complete list of values refer to Appendix 7B). In general, the major elements (Si, Al, Ti) display a trend that largely mirrors lithology and as such their vertical profile can be subdivided into the previously demarcated units. Within Unit 1, Si, Al and Ti show an oscillating trend with peaks that are usually higher than their respective averages (Si $\bar{x}$ = $58.78 \text{ ppm} \cdot 10^{-3}$, Al $\bar{x}$ = $23.28 \text{ ppm} \cdot 10^{-3}$, Ti $\bar{x}$ = $1.11 \text{ ppm} \cdot 10^{-3}$) in marlstone and argillaceous limestone beds. Conversely, limestone beds within Unit 1 show relatively lower concentration of Si, Al and Ti, i.e. below their respective average. In the interval

corresponding to Unit 2, the concentration of Si, Al and Ti simultaneously increase above their respective average, except at discrete intervals of argillaceous limestone beds, mainly at 158.02 m and 164.61 m, where values decrease below the average. A strong decrease in concentration of these elements is registered in the limestone beds corresponding to Unit 3. In particular, Al and Ti show acute declines with minimums of $4.61 \text{ ppm} \cdot 10^{-3}$ and $0.26 \text{ ppm} \cdot 10^{-3}$, respectively, followed by Si whose concentration decreases to $35.54 \text{ ppm} \cdot 10^{-3}$. On average, the concentration of Si, Al and Ti in Unit 3 represents a 19.04%, 60.57% and 57.87% percent reduction, respectively, relative to the average value of these elements in the 85.82 m studied interval. The two remaining biolimiting elements P and Fe display a vertical trend analogous to Si, Al and Ti. In fact, both P and Fe have a strong positive correlation of $r = 0.71$ and $r = 0.95$, respectively, when compared with Al. Essentially, in Unit 1, peaks in P and Fe exceed their respective

Figure 7-5 A-E) Vertical plots of major elements compared with lithology. All values are expressed in parts per thousand ($\text{ppm} \cdot 10^{-3}$). Vertical red dashed lines represent the respective element's average value. A-E) Bluish bands correspond to argillaceous limestone and marlstone intervals.

averages ($P \bar{x} = 0.24 \text{ ppm} \cdot 10^{-3}$, $Fe \bar{x} = 11.35 \text{ ppm} \cdot 10^{-3}$) in argillaceous limestone and marlstone beds. In the overlying Unit 2 interval, P and Fe show a marked increase with values that mostly stay above their individual averages. The uppermost rocks of Unit 3 display impoverished P ($\bar{x} = 0.15 \text{ ppm} \cdot 10^{-3}$) and Fe ($\bar{x} = 5.75 \text{ ppm} \cdot 10^{-3}$) concentrations, which represent a 37.5% and 49.34% decrease, relative to their respective average.

Detailed variations of RSTEs (V $\bar{x} = 37.82 \text{ ppm}$, Cr $\bar{x} = 33.87 \text{ ppm}$, Co $\bar{x} = 0.79 \text{ ppm}$, Ni $\bar{x} = 16.16 \text{ ppm}$, Cu $\bar{x} = 5.15 \text{ ppm}$, Mo $\bar{x} = 1.69 \text{ ppm}$, and U $\bar{x} = 0.95 \text{ ppm}$) are presented in Figure 7-6 (For a complete list of values refer to Appendix 7B). In the 28.08 m-interval of Unit 1, RSTEs show similar trends characterized by fluctuating values that closely follow lithologic variations. Higher values above their respective average usually occur in argillaceous limestone and marlstone beds. Conversely, lower values below the element's average usually correspond to limestone beds. The ensuing 53.81 m-interval of Unit 2 that consists predominantly of marlstones shows increased RSTE values that mostly stay above each element's respective average. The uppermost 3.93 m-interval of Unit 3 exhibits an abrupt decrease in all RSTEs. For example, V decreases to 9.62 ppm at 169.89 m, recording the lowest concentration in the entire El Pujal section. Comparing the RSTEs vertical trend with benthic fauna counts and bioturbation index reveals essentially an inverse relationship, whereby peaks in RSTEs concur with intervals of lower benthic fauna counts and lower degree of bioturbation. As an example, the concentration of V displays a strong negative correlation with benthic foraminifera ρ ($r = -0.79$), echinoid fragments ρ ($r = -0.85$) and bioturbation index ($r = -0.81$). Compared with the carbon geochemistry, RSTEs mainly display decreased values in intervals of high TIC/low TOC (limestone layers) and elevated values in intervals of low TIC/high

TOC (argillaceous limestone and marlstone layers). This relationship is exemplified by the strong negative correlation between V and TIC ($r = -0.93$) and strong positive correlation with TOC ($r = 0.75$).

In addition to their absolute values, degrees of enrichment of RSTEs (expressed as EIs) relative to background levels (OBABV) were calculated and presented in Figure 7-6H, I. Most RSTEs are enriched (values >1) in argillaceous limestone and marlstone beds, but show depleted values in limestone beds throughout this 85.82 m representing the upper part of the studied El Pujal section. Nonetheless, V is an exception, because it is enriched throughout, regardless of lithology, albeit its apparent depletion in Unit 3. On the contrary, Co and Ni are never enriched, although they show minor peaks in argillaceous limestone and marlstone beds. There is a distinct, concurrent depletion in all RSTEs coincident with the hard limestone at the onset of Unit 3. Summing the EIs ($\sum$ EIs) of each element, their interrelationship with TIC results show a strong negative correlation ($r = -0.94$). Similar relationships are recorded when $\sum$ EIs are compared with benthic foraminifera ρ ($r = -0.78$), echinoid fragment ρ ($r = -0.84$) and bioturbation index ($r = -0.85$). On the contrary, $\sum$ EIs displays a strong positive correlation with TOC ($r = 0.81$).

7.4.4 Lipid Analysis Results

Analysis via full scan GC/MS of aliphatic fractions reveals that the extractable hydrocarbons are dominated by *n*-alkanes and the acyclic isoprenoids pristane (Pr) and phytane (Ph) (Fig. 7-7). Chromatograms show a homologous series of *n*-alkanes ranging from nC_{11} to nC_{32} with a unimodal positively skewed distribution in samples taken from Unit 1 and 2, but a unimodal negatively skewed distribution in samples from Unit 3 (Fig.

Figure 7-6 A-G) Vertical plots of redox-sensitive trace elements (RSTEs) reported as absolute values in parts per million (ppm). H) Vertical plot of RSTEs enrichment indices (EI RSTEs) relative to the Organyà Basin's Average Background Value (OBABV) from Socorro and Maurrasse (2019b). I) Vertical plot of the addition of all the EIs of each element for each sample. A-I) Bluish bands correspond to argillaceous limestone and marlstone intervals.

Figure 7-7 Representative total ion chromatograms of the aliphatic fraction from three samples. Labeled peaks refer to n -alkane's carbon chain length. Peaks labeled as Pr and Ph refer to pristane and phytane, respectively.

7-7). Indications for biodegradation, such as an elevated chromatographic baseline or unresolved complex mixture (UCM) hump, were absent. To facilitate the interpretation of the n -alkanes distributions, terrigenous/aquatic ratio (TAR) values were calculated and plotted in Figure 7-8A. TAR values vary between 0.25 to 0.84, with an average of 0.37.

A shift occurs in the TAR record at the onset of Unit 3 correlative with decreasing organic carbon accumulation. Also, compared to Unit 1 and 2, the relative contribution of long-chain length ($>nC_{19}$) increases and remains significant throughout Unit 3 which yielded the highest TAR values that reach up to 0.84 (171.89 m). Values of carbon preference index (CPI) ranged from 0.93 to 1.09 ($\bar{x} = 1.03$) with the majority of the lower values (0.93-1.02) being recorded within Unit 3 (Refer to Appendix 7C). The acyclic

Figure 7-8 A) Vertical plot of the relative proportion of terrestrial to aquatic organic matter (i.e. TAR). B) Vertical plot of the relative proportion of C_{30} Gammacerane to C_{30} $17\alpha,21\beta(H)$ hopane (i.e. Gammacerane Index). C) Vertical plot of the relative proportion of C_{27} $5\alpha,14\alpha,17\alpha(H)$ sterane (20R) to C_{29} $5\alpha,14\alpha,17\alpha(H)$ sterane (20R) (i.e. C_{27}/C_{29}). A-C) Bluish bands correspond to argillaceous limestone and marlstone intervals.

isoprenoids represented by Pr and Ph are abundant in all the samples. The Pr/Ph ratios vary from 0.83 to 1.59 ($\bar{x} = 1.20$), with generally lower values (0.83-1.25) in Unit 3 (Refer to Appendix 7C). Values of isoprenoid/*n*-alkanes ratios (Pr/*n*C₁₇ vs Ph/*n*C₁₈) are relatively low as they average 0.26 and 0.22, respectively. A plot of Pr/*n*C₁₇ vs Ph/*n*C₁₈ shows most samples plotting in the region of mixed type II/III kerogen and marine type II kerogen (Fig. 7-9).

Figure 7-9 Log-log cross plot of Pristane/*n*-C₁₇ vs. Phytane/*n*-C₁₈ values of selected samples. Kerogen type fields after Shanmugam (1985) from concepts proposed by Lijmbach (1975).

Hopanes with carbon numbers ranging from C₂₇ to C₃₅ are present in all of the analyzed samples (for representative chromatograms refer to Figure 7-10A and Table 7-1). The C₂₇ hopanes (m/z 370→191) are dominated by 18 α -22,29,30-trisnorneohopane (Ts) and 17 α -22,29,30-trisnorhopane (Tm). Calculated Ts/(Ts+Tm) ratios vary between 0.58 to 0.63, with an average of 0.61 (Refer to Appendix 7C) and show a weak negative correlation with lithology (TIC) ($r = -0.21$). The C₃₀ hopanes (m/z 412→191) is dominated by C₃₀ 17 α ,21 β (H) hopane (C₃₀ $\alpha\beta$). Also, the presence of the triterpenoid alcohol, tetrahymanol (gammaceran-3 β -ol), typically referred to as gammacerane is of importance in the m/z 412→191 chromatograms. Gammacerane is present in all of the

studied samples, but with varying proportions as illustrated by the plot of the gammacerane index (gammacerane/C₃₀αβ) (Fig. 7-8B). In Unit 1 and 2 the gammacerane index displays a strong negative correlation with TIC ($r = -0.92$) and a strong positive correlation with TOC ($r = 0.90$), while in Unit 3 the gammacerane peak is barely detectible, thus leading to near zero values (Fig. 7-8B). The homohopane homologous series as summarized in Figure 7-10B (m/z 426, 440, 454, 468, 482→191) ranges from C₃₁ to C₃₅. The C₃₁ homohopane 22S/(22S+22R) isomerization ratio yields values that vary from 0.48 to 0.59 with an average of 0.55 (Table 7-2).

A range of C₂₇ to C₃₀ diasteranes and steranes occur in all of the studied samples (for representative chromatograms refer to Figure 7-10 and Table 7-1). The relative distribution of 5α,14α,17α(H) (20R) C₂₇, 5α,14α,17α(H) (20R) C₂₈ and 5α,14α,17α(H) (20R) C₂₉ steranes (αααR) varies (C₂₇ αααR $\bar{x} = 29.61\%$, C₂₈ αααR $\bar{x} = 22.54$, C₂₉ αααR $\bar{x} = 47.85$), with C₂₉ αααR always being dominant (37.65% - 55.90%). The ternary diagram plot of % C₂₇ αααR, % C₂₈ αααR and % C₂₉ αααR indicates that most samples have an estuarine to terrestrial sterane signature (Fig. 7-11). Plots of 5α,14α,17α(H) (20R) C₂₇ to 5α,14α,17α(H) (20R) C₂₉ ratio (C₂₇/C₂₉) (Fig. 7-8) display variable values (0.49-0.93 $\bar{x} = 0.66$) in Unit 1 and 2 that inversely correlate with TOC ($r = -0.87$), while Unit 3 contains almost no variability (0.54 - 0.57) and consistently lower values ($\bar{x} = 0.55$). Isomerization of the C-20 stereocenter in the 5α,14α,17α(H) C₂₉ sterane expressed as the C₂₉ 20S/(20S+20R) ratio varies from 0.42 to 0.59 and averages 0.52 (Table 7-2). Beta-isomerization at C-14 and C-17 in the 5α,14α,17α(H) C₂₉ 20S and 20R sterane expressed as the C₂₉ ββ/(ββ+αα) ratio varies from 0.56 to 0.66 and averages 0.62 (Table 7-2).

Figure 7-10 MRM transition profiles from a representative sample showing the distribution of various hopanes, steranes and diasteranes. Refer to Table 7-1 for peak identification.

Table 7-1 Identified biomarkers compounds. The numbers next to the respective compounds refers to the numbered peaks in Figure 7-10.

Hopanes (<i>m/z</i> 191)	Steranes and Diasteranes (<i>m/z</i> 217)
1. 18 α -22,29,30-Trisnorhopane (Ts)	17. C ₂₇ 13 β ,17 α (H) diasterane (20S)
2. 17 α -22,29,30-Trisnorhopane (Tm)	18. C ₂₇ 13 β ,17 α (H) diasterane (20R)
3. C ₂₉ 17 α ,21 β (H) hopane	19. C ₂₇ 13 α ,17 β (H) diasterane (20S)
4. 18 α -30-norneohopane (29Ts)	20. C ₂₇ 13 α ,17 β (H) diasterane (20R)
5. C ₃₀ 17 α ,21 β (H) hopane	21. C ₂₇ 5 α ,14 α ,17 α (H) sterane (20S)
6. C ₃₀ Gammacerane	22. C ₂₇ 5 α ,14 β ,17 β (H) sterane (20R)
7. C ₃₁ 17 α ,21 β (H) homohopane (22S)	23. C ₂₇ 5 α ,14 β ,17 β (H) sterane (20S)
8. C ₃₁ 17 α ,21 β (H) homohopane (22R)	24. C ₂₇ 5 α ,14 α ,17 α (H) sterane (20R)
9. C ₃₂ 17 α ,21 β (H) homohopane (22S)	25. C ₂₈ 13 β ,17 α (H) diasterane (20S) isomeric peaks (24S and 24R)
10. C ₃₂ 17 α ,21 β (H) homohopane (22R)	26. C ₂₈ 13 β ,17 α (H) diasterane (20R) isomeric peaks (24S and 24R)
11. C ₃₃ 17 α ,21 β (H) homohopane (22S)	27. C ₂₈ 13 α ,17 β (H) diasterane (20S)
12. C ₃₃ 17 α ,21 β (H) homohopane (22R)	28. C ₂₈ 13 α ,17 β (H) diasterane (20R) isomeric peaks (24S and 24R)
13. C ₃₄ 17 α ,21 β (H) homohopane (22S)	29. C ₂₈ 5 α ,14 α ,17 α (H) sterane (20S) isomeric peaks (24S and 24R)
14. C ₃₄ 17 α ,21 β (H) homohopane (22R)	30. C ₂₈ 5 α ,14 β ,17 β (H) sterane (20R)
15. C ₃₅ 17 α ,21 β (H) homohopane (22S)	31. C ₂₈ 5 α ,14 β ,17 β (H) sterane (20S)
16. C ₃₅ 17 α ,21 β (H) homohopane (22R)	32. C ₂₈ 5 α ,14 α ,17 α (H) sterane (20R)
	33. C ₂₉ 13 β ,17 α (H) diasterane (20S)
	34. C ₂₉ 13 β ,17 α (H) diasterane (20R)
	35. C ₂₉ 13 α ,17 β (H) diasterane (20S)
	36. C ₂₉ 13 α ,17 β (H) diasterane (20R)
	37. C ₂₉ 5 α ,14 α ,17 α (H) sterane (20S)
	38. C ₂₉ 5 α ,14 β ,17 β (H) sterane (20R)
	39. C ₂₉ 5 α ,14 β ,17 β (H) sterane (20S)
	40. C ₂₉ 5 α ,14 α ,17 α (H) sterane (20R)
	41. C ₃₀ 13 β ,17 α (H) diasterane (20S)
	42. C ₃₀ 13 β ,17 α (H) diasterane (20R)
	43. C ₃₀ 5 α ,14 α ,17 α (H) sterane (20S)
	44. C ₃₀ 5 α ,14 β ,17 β (H) sterane (20R)
	45. C ₃₀ 5 α ,14 β ,17 β (H) sterane (20S)
	46. C ₃₀ 5 α ,14 α ,17 α (H) sterane (20R)

Table 7-2 Values of calculated biomarker thermal maturation indices.

Sample ID	Height (m)	C ₃₁ 22S/(22S+22R)	C ₂₉ 20S/(20S+20R)	C ₂₉ $\beta\beta$ /($\beta\beta$ + $\alpha\alpha$)
C-17-256	171.16	0.56	0.42	0.58
C-17-254	169.89	0.54	0.54	0.65
C-17-253	168.87	0.58	0.54	0.66
C-17-242	160.3	0.54	0.54	0.65
C-17-226	146.61	0.52	0.48	0.62
C-17-204	128.1	0.59	0.42	0.60
C-17-183	110.79	0.56	0.57	0.60
C-17-170	100.1	0.48	0.55	0.64
C-17-157	89.51	0.55	0.59	0.62
C-17-152	86.07	0.53	0.52	0.56
Average		0.55	0.52	0.62

Figure 7-11 Ternary diagram showing the sterane composition of selected samples and their relationship with source input. Fields after Shanmugam (1985) from concepts proposed by Huang and Meinschein (1979).

7.4.5 Bulk and Clay Mineralogy

Results of the bulk mineral content of 10 samples from representative lithologies of the El Pujal section are presented in Table 7-3. Their composition consists mainly of calcite (57% - 73%, $\bar{x}$ = 66%), quartz (9% - 15%, $\bar{x}$ = 12%), clay minerals (8% - 12%, $\bar{x}$ = 9%), with minor amounts of siderite (2% - 7%, $\bar{x}$ = 4%), P-feldspar (2% - 5%, $\bar{x}$ = 3%), K-feldspar (1% - 4%, $\bar{x}$ = 2%), pyrite/marcasite (1% - 3%, $\bar{x}$ = 2%) and dolomite (1% -

Table 7-3 Bulk mineralogical composition of selected samples distributed throughout the studied interval.

Sample ID	Height (m)	Clay	Quartz	K-feldspar	P-feldspar	Calcite	Dolomite	Siderite	Pyrite/Marcasite
C-17-257	171.89	9%	11%	2%	2%	72%	1%	3%	1%
C-17-255	170.49	10%	12%	1%	2%	69%	1%	2%	3%
C-17-249	166.81	9%	14%	4%	3%	64%	1%	4%	1%
C-17-217	139.39	8%	15%	3%	3%	65%	1%	4%	1%
C-17-197	122.27	8%	14%	2%	2%	65%	2%	4%	3%
C-17-183	110.79	9%	10%	2%	2%	73%	1%	2%	1%
C-17-180	108.19	12%	12%	2%	2%	66%	1%	4%	1%
C-17-170	100.1	9%	11%	3%	3%	67%	1%	3%	2%
C-17-157	89.51	9%	14%	3%	5%	57%	2%	7%	3%
C-17-152	86.07	12%	9%	3%	3%	66%	1%	4%	2%

2%, $\bar{x} = 1\%$). The overall averages for each lithologic Unit indicate only minor ($\leq 5\%$) temporal variability of the bulk mineral content (Fig. 7-12). Appreciable shifts ($\geq 3\%$) occur only in the quartz and calcite contents. Quartz shows a 4% increase between Unit 1 (11%) and Unit 2 (15%) and a decrease of 3% between Unit 2 (15%) and Unit 3 (12%) (Fig. 7-12). Similarly, calcite increases by 5%, but only between Unit 2 and Unit 3 (Fig. 7-12).

Figure 7-12 Pie diagrams of average bulk and clay mineralogy for Units 1-3. For a comprehensive bulk mineralogical composition of the analyzed samples, refer to Table 7-3.

Specific clay mineral constituents of the El Pujal sediments were also determined for the 10 samples analyzed for bulk mineral content. The results shown in Figure 7-13 reveal that the clay fraction is dominated by illite ($\bar{x} = 67\%$) with percentages that fluctuate between 55% and 78%. Kaolinite ($\bar{x} = 13\%$) represents the next most abundant clay mineral, but unlike illite it has a much smaller variability (11%), oscillating between 7% and 18%. Chlorite follows in abundance with an average of 12% and values that

Figure 7-13 Temporal variation of clay mineral content compared with lithology.

oscillate between 6% and 15%, a range of 9%. Smectite constitutes the smallest portion (9%) of the clay minerals, yet a relatively high range (15%) of values that vary from 4% to 19% characterizes it. The trends in the clay mineral averages for each lithologic Unit (Fig. 7-12) shows a marked 11% decrease in illite content between Unit 2 and Unit 3, coeval with a 6% increase in smectite.

7.5 Discussion

7.5.1 Paleoenvironmental Conditions: Integration of Stratigraphy and Geochemistry

The distinctive field-scale characteristics of facies corresponding to Unit 1 (86.07 m - 114.15 m) (Fig. 7-2) in the present study of the El Pujal section include a repetitive series of alternating indurated limestones and softer argillaceous limestones to marlstones, suggestive of recurring different paleoenvironmental conditions. The microfacies reveal that only the softer argillaceous limestone and marlstone beds include frequent dispersive pyritized allochems, low bioturbation indices (~ 3 , indicative of restricted burrowing activity) and impoverished benthic faunal counts (Fig. 7-3A, B, C), which all imply oxygen-deficient conditions at these times (Wignall and Myers, 1988; Taylor and Goldring, 1993). Coeval peaks in TOC (Fig. 7-4B) that demonstrate preservation of OM together with enrichment of most RSTEs (Fig. 7-6H) support the assumption of episodic oxygen-restricted conditions in the basin, whereas the limestone beds indicate periods of higher ventilation. In addition to the concurrence of these oxygenation proxies, major elemental contents and biolimiting elements further show a striking pattern of synchronicity with peaks in Si, Al, and Ti (Fig. 7-5A, B, C), coeval with those of Fe and P (Fig. 7-5D, E), and higher contribution of OM from terrestrial sources (Fig. 7-8A, C), thus suggesting coincident intensified pulses of fluvial discharge

and nutrient loads. Under such conditions, freshwater runoff may have resulted in density stratification of the water column preventing vertical mixing of oxygen depleted bottom waters with more oxygenated surface waters. The biomarker results also show concurrent peaks of gammacerane (Fig. 7-8B), therefore providing further corroborative evidence for stratification of the water column (Harvey and Mcmanus, 1991; Sinninghe Damsté et al., 1995). As previously discussed for the lower ~ 85 m portion of the El Pujal section (Socorro and Maurrasse, 2019a,b), the present results also permit to infer that Unit 1 represents an interval of variable fluvial fluxes possibly related to climatic fluctuations similar to those reported in the Mediterranean area during the latest Miocene (Mayser et al., 2017) and the Pleistocene last interglacial (Wu et al., 2018). These conditions may thus explain the alternating lithology with limestones representing the least terrestrially influenced endmember and marlstones representing points of highest terrestrial influences.

The subsequent Unit 2 can be interpreted to represent a facies transition consisting predominately of marlstone between 114.15 m and 167.96 m (Fig. 7-2). It is the upward extension of alternating lithologies previously studied in the lower part of the section (~ 85 m-interval) (Socorro and Maurrasse, 2019a,b) which is also continuous into Unit 1 of the present study (Fig. 7-2). Unit 2 consists of homogenous microfacies including mostly pyritized allochems (Fig. 7-2C), reduced benthic fauna counts and lower degree of bioturbation (~ 3) (Fig. 7-3A, B, C), analogous to the marlstone intervals in Unit 1. The change in facies occurs simultaneously with further sustained increase in TOC ($\bar{x}$ = 1.01%), and RSTEs. Together, these data suggest continuous oxygen-deprived conditions, but without a fully anoxic phase, as benthic fauna while relatively reduced,

are still present throughout. Concurrent lasting terrigenous fluxes are implied as evidenced by elevated major elements (Si, Al, Ti) (Fig. 7-5A, B, C), biolimiting elements (Fe, P) (Fig. 7-5D, E) and higher terrestrial OM contents (Fig. 7-8A, C). Freshwater discharge must have been persistent during this time as indicated by continually elevated gammacerane indices (Fig. 7-8B). Thus, these results suggest an increase in runoff apparently related to established humid continental conditions that prevailed in this interval causing strong, quasi-permanent eutrophic surface waters in the Organyà Basin. That is not to say, however, that recurrent periods of dry climatic conditions did not develop during this interval in the Organyà Basin as presumably they did (refer to Figure 7-2A Unit 2 – notice intervals of argillaceous limestones). However, it appears that if they did occur, they were of short duration and their signal, typified by the deposition of OM-lean limestones, is not perceivable as it was likely subdued by the amplified signal from more persistent wet climate intervals.

Hard limestones associated with Unit 3 (167.96 m - 171.89 m) represent a sharp change in lithology (Fig. 7-2) as the microfacies gradually shifts to coarser grain, highly bioturbated (>5) packed biosparites (Fig. 7-2C; Fig. 7-3C). These changes indicate an increase in energy conditions and a shift towards more aerobic bottom waters. The biogenic assemblage is composed of abundant benthic foraminifera, echinoid fragments, sponge spicules, scarce planktonic foraminifera and varying amounts of unidentifiable skeletal detritus (Fig. 7-2C). The change in allochem components occurs together with decreases in TOC ($\bar{x}$ = 0.47%) (Fig. 7-4B) and depletion of all RSTEs relative to background values (Fig. 7-6H), which attests to increases in oxygen content. Drier climatic conditions can be inferred on the adjacent land masses as suggested by an

increase in smectite ($\bar{x} = 14\%$), but decreases in illite ($\bar{x} = 58\%$) (Fig. 7-12), Si, Al, and Ti (Fig. 7-5A, B, C) (Singer, 1984; Eslinger and Pevear, 1988; Bühmann and Schoeman, 1995). We may also postulate that simultaneous decreases in biolimiting elements Fe and P (Fig. 7-5D, E) resulted in a decline of *in-situ* primary production (Fig. 7-7; Fig. 7-8 A, C). Furthermore, gammacerane indices also drop to near zero (Fig. 7-8B), revealing an apparent termination of density stratification of the water column in the Organyà Basin.

7.5.2 Thermal Maturity Assessment

Assessing the thermal history of the sediment is a critical step before attempting interpretations of the organic geochemical data, because it can affect the interpretation of OM sources as well as the stable carbon isotope data ($\delta^{13}\text{C}_{\text{org}}$) (Philippi, 1965; Tissot, 1974; Tissot Clayton, 1991; Clayton and Bjorøy, 1994; Tang et al., 2005; Peters et al., 2005, 2007). Here we rely on hopane and sterane biomarker parameters to define the magnitude of thermal maturation in the El Pujal section. Our premise relies on established evidence that thermal maturation causes predictable transformation of the original hopanoid and sterol stereochemical configuration (Mackenzie et al., 1980; Seifert and Moldowan, 1980; Curiale et al., 1989; Peters et al., 2005, 2007). For instance, the biological form of the C_{31} homohopane contains a C-22 chiral center with a 22R configuration, which during thermal maturation converts to the 22S isomer (Curiale et al., 1989; Peters et al., 2007). Increasing thermal maturity increases the C_{31} homohopane 22S/(22S+22R) ratio from 0 up to an equilibrium value of 0.6 (Seifert and Moldowan, 1986; Peters et al., 2007)). Analyzed samples at El Pujal show that the C_{31} homohopane 22S/(22S+22R) has an average value of 0.55 (Table 7-2), below the established equilibrium endpoint. Similarly, as thermal maturity increases the isomerization at the C-

20 position in the C₂₉ 5 α ,14 α ,17 α (H) sterane converts from a 20R configuration in biologically derived steroid precursors to a 20S isomer, thus increasing the 20S/(20S+20R) ratio from 0 to an equilibrium value of 0.55 (Seifert and Moldowan, 1986; Peters et al., 2007). The C₂₉ 20S/(20S+20R) values for the El Pujal section averages 0.52 (Table 7-2), which is also below the equilibrium value of this parameter. Beta-isomerization at the asymmetric centers of the C-14 and C-17 in the C₂₉ 5 α ,14 α ,17 α (H) 20R and 20S sterane provides an additional constrain of thermal maturity, because the less stable 5 α ,14 α ,17 α (H) configuration converts to the more stable 5 α ,14 β ,17 β (H) configuration. Abundances of the 5 α ,14 α ,17 α (H) configuration typically decrease relative to the 5 α ,14 β ,17 β (H) configuration with increasing thermal maturity causing the C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio to increase from 0 to 0.71 (Seifert and Moldowan, 1986; Peters et al., 2007). The El Pujal section has C₂₉ $\beta\beta/(\beta\beta+\alpha\alpha)$ values that average 0.62 (Table 7-2), in accord with previous maturity parameters since it is also below the endpoint equilibrium value. These results indicate that sediments of the El Pujal section experienced temperatures of ~ 50°C to 60°C, which falls within the onset of the oil window (Peters et al., 2007). The consistency between the analyzed biomarker thermal maturity indicators thus suggests that thermal maturity should not be an issue when interpreting the organic geochemical results.

7.5.3 OM Sources and Temporal Variability

Previous studies on older sediments of the Organyà Basin associated with the El Pui sequence confirmed their hemipelagic setting (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) during a time influenced by episodes of intensified terrestrial influx, as also demonstrated in the succeeding deposits of the lower

portion of the El Pujal section (Socorro and Maurrasse, 2019a,b). Owing to these findings, OM source identification becomes a more involved task since these marine settings preserve a complex signal that is influenced by distinct, but connected ecosystems that include rivers, estuaries and the ocean (Méjanelle and Laureillard, 2008; Ramaswamy et al., 2008; Carreira et al., 2010; Schmidt et al., 2010; Bauer et al., 2013; Cordeiro et al., 2018). Despite this tangled archive, the molecular biomarker approach, especially from lipids (*n*-alkanes, hopanes and steranes), provides the most robust proxy for identifying OM sources because of their phylogenetic specificity, which in some cases can even identify particular class of organisms (e.g. types of bacteria and plants), further complemented by the relative diagenetic and chemical stability of some of these compounds (Cranwell, 1973; Giger et al., 1980; Meyers, 1997; Forster et al., 2004; Peters et al., 2005; 2007; Brocks and Summons, 2014). Because most living organisms have specific environmental requirements, thus characterizing the source of OM in a paleodepositional system can provide additional insights about the paleoenvironmental conditions present during deposition.

The *n*-alkanes distribution of the present study in the upper 85.82 m of the El Pujal section reveals a homologous series that spans from nC_{11} to nC_{32} (Fig. 7-7). These results signify a mixed supply of OM derived from varied sources including bacteria and phytoplankton by *in-situ* production ($\leq nC_{19}$), and allochthonous material originating from aquatic macrophytes/*sphagnum* species (nC_{20} - nC_{25}) and, terrestrial vegetation ($>nC_{25}$) (Eglinton and Hamilton, 1967; Han et al., 1968; Winters et al., 1969; Gelpi et al., 1970; Blumer et al., 1971; Cranwell, 1984; Viso et al., 1993; Riederer and Markstädter, 1996; Baas et al., 2000; Ficken et al., 2000; Mead et al., 2005; Schirmer et al., 2010; Gao

et al., 2011). The values of Pristane/ n C₁₇ vs Phytane/ n C₁₈ further provide corroborating evidence, as they show that the samples plot within the marine type II kerogen to mixed type II/III kerogen indicative of marine and terrestrial OM sources (Fig. 7-9). Arguably, this ratio can be problematic because bacteria generally degrade the more labile n -alkanes before the isoprenoids. However, the almost non-existent UCM displayed in the chromatograms (Fig. 7-7) indicates that biodegradation can be ruled out (Wenger and Isaksen, 2002; Peters et al., 2005). Additionally, steranes, a class of tetracyclic triterpanes originating from the diagenetic alteration of sterols derived from the cell membranes of eukaryotic organisms were detected (Fig. 7-10B) (Nes, 1974; Mackenzie et al., 1982; Moldowan et al., 1985; Hartmann, 1998; Volkman, 2003, 2005; Peters et al., 2005; Dufourc, 2008). The presence of all three of the $\alpha\alpha\alpha$ -20R epimers of C₂₇, C₂₈ and C₂₉ sterane originating from various eukaryotic sources including zooplankton, phytoplankton and terrestrial vegetation provides further evidence in support of this conclusion (Fig. 7-10B and Table 7-1). A dominant estuarine to terrestrial OM signature is recorded (Fig. 7-11) in the ternary distribution plot of the C₂₇, C₂₈, and C₂₉ $\alpha\alpha\alpha$ -20R steranes, a useful metric to determine OM source input and depositional environment, thus attesting to the mixed contribution of OM sources to the TOC (Huang and Meinschein, 1979). Hopanoids, a class of pentacyclic triterpenoids found in the lipid membrane of various prokaryotes, including oxic-heterotrophic bacteria, anaerobic sulfate-reducing bacteria and cyanobacteria were also detected (Fig. 7-10A), hence implying that bacteria were also an important source of OM input in the sediments associated with the El Pujal section (Ourisson et al., 1979, 1982, 1987; Ourisson and

Rohmer, 1992; Sinninghe Damsté et al., 2004; Härtner et al., 2005; Blumenberg et al., 2006; Peters et al., 2007).

The complex nature of OM at El Pujal complicates appraisal of the temporal variability in the relative contribution of autochthonous marine versus allochthonous OM sources. Accordingly, we used taxonomically diagnostic biomarker indices for these two end-member OM sources, including the terrestrial to aquatic ratio (TAR) and the ratio of the $\alpha\alpha\alpha$ -20R C₂₇ sterane to $\alpha\alpha\alpha$ -20R C₂₉ sterane (C₂₇/C₂₉). Their usefulness stems from the distribution of carbon as for example, *n*-alkanes with more than ~ 25 carbon occur in epicuticular leaf wax of terrestrial plants where they contribute to hydrophobic properties and as a barrier from the external environment (Post-Beittenmiller, 1996; Riederer and Markstädter, 1996; Jetter et al., 2006). By contrast, *n*-alkanes with odd carbon numbers between *n*C₁₅ and *n*C₁₉ are characteristically enriched in phytoplankton and bacteria, which encompasses the bulk of the *in-situ* produced biomass (Winters et al., 1969; Blumer et al., 1971; Cranwell, 1984). A similar relationship can be derived from the $\alpha\alpha\alpha$ -20R sterane homologous series, although not as certain as that derived for *n*-alkanes (Volkman, 1986, 1988). It relies on the observation that C₂₇ homologs are mainly of autochthonous origins while the C₂₉ homologs are mostly associated with terrestrial vegetation (Huang and Meinschein, 1979; Volkman, 1986; Volkman et al., 1998; Volkman, 2003; Peters et al., 2005; Kim et al., 2016; Duan et al., 2017). Thus, a ratio between high molecular weight to low molecular weight *n*-alkanes (i.e. TAR) and $\alpha\alpha\alpha$ -20R C₂₇ to C₂₉ steranes (C₂₇/C₂₉) can provide an effective proxy to discriminate the relative contribution from these two end-member OM sources. At El Pujal, Unit 1 and Unit 2 are characterized by fluctuating TAR paralleling with lithology, whereby higher

values are associated with OM-rich, argillaceous limestone and marlstone intervals (Fig. 7-8A). Thus, coeval increases in the proportion of C_{29} to C_{27} $\alpha\alpha\alpha$ -20R steranes (otherwise a decrease in C_{27}/C_{29}) (Fig. 7-8C) and Si, Al and Ti content (Fig. 7-5A, B, C) suggest enhanced fluvial pulses during the deposition of OM-rich lithology. However, a subsequent increase in TAR and decrease in C_{27}/C_{29} within Unit 3 (Fig. 7-8A, C) is inconsistent with terrigenous fluxes because that interval also shows a sharp decreasing trend in Si, Al, Ti and biolimiting elements Fe and P (Martin and Fitzwater, 1988; Krom et al., 1991; Zohary and Robarts, 1998; Boyd et al., 2000; Diaz et al., 2001; Gervais et al., 2002; Coale et al., 2004; Blain et al., 2007) (Fig. 7-5). Moreover, the clay mineral assemblages show concurrent increase in smectite and decrease in illite content (Fig. 7-12), which lend support to a shift toward a dryer climate (Singer, 1984; Eslinger and Pevear, 1988; Bühmann and Schoeman, 1995). To resolve these paradoxical results we postulate that since fluvial fluxes are the main transporting agent of Fe and P in the Organyà Basin (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro and Maurrasse, 2019a,b), therefore their decrease would have caused limited *in-situ* primary production of OM, thereby indirectly increasing the TAR and decreasing the C_{27}/C_{29} ratio. This apparent divergence further highlights the limitation of ratio indices, and attests to the necessity of incorporating the multiproxy approach when conducting comparable investigations.

7.5.4 Biostratigraphy and Stable Carbon Isotope Stratigraphy

Recent biostratigraphic studies of numerous Lower Aptian sequences concur that the occurrence of the index planktonic foraminifer, *L. cabri* parallels the OAE1a interval (e.g., Magniez-Janin et al., 1997; Aguado et al., 1999; Bellanca et al., 2002; Verga and

Premoli Silva 2002; Erba, 2004; Coccioni et al., 2006; Heldt et al., 2008; Moullade et al., 2015). Thin section analysis of the uppermost 85.82 m-interval at El Pujal reveals the presence of *L.cabri* in Unit 1 and 2 of the section which concur with previous findings that provide a chronostratigraphic positions of the El Pujal coeval with OAE1a (Socorro and Maurrasse, 2019a,b). The absence of *L.cabri* in Unit 3 is possibly related to ecological restraints induced by shallowing of the basin at this time as previously discussed.

[illegible]

As demonstrated in previous studies the combined $\delta^{13}\text{C}_{\text{org}}$ results at El Pujal (Socorro and Maurrasse, 2019a,b) (Fig. 7-14) is continuous with the neighboring El Pui section (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016) (Fig. 7-14) and they coincide with OAE1a. The present results further corroborate

the precise position of the El Pujal section as concurrent with carbon-isotope segment C5 (Menegatti et al., 1998). The combined high-resolution $\delta^{13}\text{C}_{\text{org}}$ data (Socorro and Maurrasse 2019b) also revealed six apparent subsegments of carbon-isotope segment C5 (C5-a to C5-f) prior to the pronounced negative inflection heralding the end of that segment seen elsewhere (Fig. 7-14). The $\delta^{13}\text{C}_{\text{org}}$ results of the present study complete the carbon isotope curve of this expanded section as the positive trend of subsegment C5-f up at 166.11 m reaches its maximum value (-23.91‰). Hence, the positive excursion characteristic of carbon isotope segment C5 in the Organyà Basin extends over 90.89 m (75.22 m – 166.11 m) (Fig. 7-14F). The closing distinctive negative shift to -25.31‰ (Fig. 7-14F) can be considered an additional subsegment (C5-g) which extends 5.78 m (166.11 m – 171.89 m). This remarkable negative excursion of the $\delta^{13}\text{C}_{\text{org}}$ curve is a robust feature that permits explicit correlation of the El Pujal section with sections elsewhere in the Tethyan realm (Fig. 7-14) (Aguado et al., 2014a,b) (Fig. 7-14A), Roter Sattel and Cismon (Menegatti et al. (1998) (Fig. 7-14B, C), Angles (Bodin et al., 2015), Gorgo a Cerbara (Li et al., 2016), Djebel Serdj (Heldt et al., 2008), the Basque-Cantabrian Basin (Fig. 7-15), Cuchía (García-Mondéjar et al., 2015), Igaratza (Millán et al., 2011), Madotz (Gaona-Narvaez et al., 2013)..

A similar negative excursion is also reported in the Santa Rosa Canyon in Mexico (Bralower et al., 1999; Li et al., 2008), Comanche Platform in the northern Gulf of Mexico (Phelps et al., 2015), and in the central Pacific Ocean at Deep Sea Drilling Project (DSDP) Site 463 (Ando et al., 2008), among others. The global occurrence of the negative excursion at the close of carbon isotope segment C5 thus suggests a causal mechanism that affected the global carbon reservoir. The worldwide significance of the

signal is further recorded in coeval lacustrine deposits (Zhang et al., 2016), confirming its effect on the ocean/atmosphere system. Sources of ^{13}C depleted CO_2 such as from volcanic emissions ($\delta^{13}\text{C} \sim -5\text{‰}$) and/or from abrupt release of methane hydrates ($\delta^{13}\text{C} \sim -60\text{‰}$) (Kvenvolden, 1993) have been postulated as potential causes of these negative shifts for similar excursions (e.g., Larson and Erba, 1999; Hesselbo et al., 2000; Jahren et al., 2001, 2005; Beerling et al., 2002; de Wit et al., 2002; van Breugel et al., 2007; Méhay et al., 2009; McInerney and Wing, 2011; Socorro et al., 2017)). Since the emplacement of massive LIPs (e.g. Ontong Java-Manihiki-Hikurangi plateau) (Larson, 1991; Tarduno et al., 1991; Ingram et al., 1994; Tejada et al., 2009) and massive volcanism in Asia (e.g. Songliao Basin volcanism) (Wang et al., 2002; 2016) are coeval with the development of OAE1a, volcanic CO_2 release in pulses of different magnitudes and duration may be invoked as the driving mechanism for the worldwide occurrences of various negative CIE during OAE1a, including those of carbon-isotope segment C2 (Socorro et al., 2017), C3 (Menegatti et al., 1998; Tejada et al., 2009; Charbonnier and Föllmi, 2017) and C5. Dissociation of methane hydrates is an additional possible factor; however, this mechanism is more likely related to large-scale negative CIEs ($\sim > -3.5\text{‰}$) of short duration ($\sim < 10,000$ yrs) as for example during the Paleocene Eocene Thermal Maximum (Kirtland Turner and Ridgwell, 2016).

Figure 7-14 A-E) Chemostratigraphic correlation based on $\delta^{13}\text{C}_{\text{org}}$ of the El Pujal section with other sections: La Frontera (Aguado et al., 2014a,b), Roter Sattel (Menegatti et al., 1998), Cison (Menegatti et al., 1998) and El Pui (Sanchez-Hernandez and Maurrasse, 2016). The C segments correspond to the subdivisions proposed by Menegatti et al. (1998). The yellow star marks the highest value within segment C5 and corresponds to equivalent points in each section. The gray band indicates the position of OAE1a or its equivalent for each section. F) Plot of El Pui and El Pujal $\delta^{13}\text{C}_{\text{org}}$ data with identical vertical and horizontal scales. For a detailed description of labeled subsegments C5-a through C5-g refer to the discussion section.

Evaluating the negative CIE range from the most positive value of segment C5 (Fig. 7-14, Point marked with a star) to the most negative value recorded at the transition from segment C5 to C6 reveals that the amplitude is noticeably different from one section to another (Fig. 7-14). For instance, in the La Frontera section (Fig. 7-14A, Spain) the most positive value of segment C5 ($\sim -22.5\text{‰}$) occurs at ~ 7.5 m, while the transition to segment C6 is at ~ 7.9 m with a value of $\sim -25\text{‰}$, thus representing a -2.5‰ shift. At Roter Sattel (Fig. 7-14B, Switzerland) the most positive value ($\sim 25\text{‰}$) is recorded at ~ 5.5 m and the negative shift to $\sim -25.6\text{‰}$, signaling the end of segment C5 comes immediately after ~ 5.6 m, hence recording a -0.6‰ shift. In the Cismon section (Fig. 7-14C, Italy) the positive plateau ($\sim -23.6\text{‰}$) occurs at ~ 263.34 m and the minimum ($\sim -25.3\text{‰}$) occurs at ~ 262.13 m, giving an amplitude of -1.7‰ . At El Pujal (Fig. 7-14E, F) the peak of the short-lived positive CIE of segment C5 (-22.55‰) appears concurrent with the end of subsegment C5-b (Fig. 7-14F) (Socorro and Maurrasse, 2019b) and the most negative value (-25.31‰) appears at 171.89 m, which marks the end of subsegment C5-g and conclude segment C5. The amplitude of the negative CIE at El Pujal thus represents a -2.76‰ shift, comparable to the value recorded at La Frontera (-2.5‰), but higher than at Roter Sattel (-0.6‰) and Cismon (-1.7‰). The differences in amplitude may be related to local modulating factors such as source of OM, biological fractionation, climate, thermal maturation, among others as the results of these studies suggest. Further detailed geochemical characterization of these other sections should shed more light on the causal mechanisms associated with these different sedimentary basins. Concerning El Pujal, the cause of the amplified negative shift (-2.76‰) can be postulated based on the reliability of the biomarker thermal maturity indicators that are consistently below their

respective equilibrium values (Table 7-2), hence effects of thermal overmaturity can be ruled out (Clayton, 1991). The OM at EL Pujal consists mainly of a mixture of marine and terrestrial OM (Fig. 7-7; Fig. 7-9; Fig. 7-11), each with differing $\delta^{13}\text{C}_{\text{org}}$ values (e.g. marine $\delta^{13}\text{C}_{\text{org}} = \sim -21\text{‰}$ (Wainright and Fry, 1994); terrestrial $\delta^{13}\text{C}_{\text{org}} = \sim -26\text{‰}$ to $\sim -28.5\text{‰}$ (Bender, 1971; Boutton, 1991; Dawson et al., 2002; Fry, 2006; Kohn, 2010)), whose combined averaged values is the resultant measured $\delta^{13}\text{C}_{\text{org}}$. Therefore, a decrease in marine primary productivity in the uppermost 3.93 m of Unit 3, a source of OM with more positive $\delta^{13}\text{C}_{\text{org}}$ values may explain the amplified negative CIE in the Organyà Basin as recorded at El Pujal at end of carbon-isotope segment C5.

7.5.5 Sedimentation Rate during Carbon Isotope Segment C5

The Organyà Basin developed as a narrow marginal basin resulting from extensional faulting generated from the sinistral translation of Iberia relative to Eurasia concurrent with the opening of the North Atlantic and the Bay of Biscay (Van der Voo, 1969; Berástegui et al., 1990; Srivastava et al., 1990; Olivet, 1996; Vergés and García-Senz, 2001; García-Senz., 2002; Vergés et al., 2002; Sibuet et al., 2004; Gong et al., 2008, 2009; Oliva-Urcia et al., 2011; Vacherat et al., 2017). Increased subsidence rates during the Aptian provided ample accommodation space for deposition (Berástegui et al., 1990; García-Senz., 2002; Bernaus et al., 2003; Gong et al., 2008, 2009). Moreover, increases in continental weathering and runoff induced by intensified hydrological cycles in response to global greenhouse conditions at that time (e.g., Dumitrescu et al., 2006; Blättler et al., 2011; Föllmi, 2012; Lechler, 2015), heightened transport of continental material and nutrient loads into the basin (Sanchez-Hernandez et al., 2014; Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro and Maurrasse, 2019a,b). These regional

and global forcing factors resulted in high sediment accumulation rates (e.g ~ 27 cm/kyr in Gong et al., 2008) as attested by an expanded interval for carbon-isotope segments C2 (Sanchez-Hernandez and Maurrasse, 2014, 2016; Socorro et al., 2017) and C5 herein (0 - 171.89 m) (Fig. 7-14F), which expands a thickness of 200.49 m including the uppermost 28.6 m (211.40 m – 240 m) (Fig. 7-14F) of the El Pui section.

To estimate the bulk sedimentation rate during carbon-isotope segment C5 in the Organyà Basin based on the suggested duration of this segment as established by Li et al. (2008) and Malinverno et al. (2010) using spectral analysis of orbital cycles and orbital tuning of high-resolution records. Assuming a duration of 570 kyr (Li et al., 2008), the approximate dry bulk accumulation rate for the 200.49 m of segment C5 is 35.17 cm/kyr. Alternatively, a duration of 510 ± 70 kyr (Malinverno et al., 2010) gives 39.31 cm/kyr (at 510 kyr) and 34.57 cm/kyr (at 580 kyr); whereas a lower value of 440 kyr yields 45.57 cm/kyr. An overall average of 540 kyr give an estimated dry bulk sedimentation rate of about 37.13 cm/kyr. To underscore the magnitude of the accumulation rates in the Organyà Basin, as compared to wet accumulation rates in similar known settings, we apply a correction factor for compaction history with an estimate of the changes in porosity with depth. The original thickness of a sedimentary unit (T_O) and any time after (T_N) is related to the change in porosity of the sediment (van Hinte, 1978):

$$T_O = \frac{(1 - \Phi_N)T_N}{1 - \Phi_O}$$

where Φ_O is the original porosity and Φ_N is the porosity at any time after. Given that comparable hemipelagic sediments yield porosity in the range of 40% to 67% with typical values at 56% (Edgar et al., 1973), we chose this value (56%) as the original

porosity (i.e. Φ_O). In the absence of actual porosity data for El Pujal (i.e. Φ_N), we may use reported porosity versus depth models for similar lithology (e.g., Mallon and Swarbrick, 2002 and reference therein). The burial depth was extrapolated from the biomarker thermal maturation data that suggest a thermal history of $\sim 60^\circ\text{C}$. Assuming a relatively high geothermal gradient ($30^\circ\text{C}/\text{km}$), which is not uncommon for pull-apart analogs with closely related physiographic conditions to the Organyà Basin (e.g., Bohai Basin: Hu et al., 2001), the estimated burial depth is ~ 2 km. Assuming that all the changes of porosity with depth result from compaction, on average, comparable carbonate-rich hemipelagic sediments decrease in porosity to $\sim 25\%$ (i.e. Φ_N) when compacted to similar depths ~ 2 km (e.g. North Sea: Mallon and Swarbrick, 2002). Thus, based on these criteria, the combined results for segment C5 in the Organyà Basin yields an estimated original thickness (T_O) of 341.74 m. Taking an average duration for carbon-isotope segment C5 of 540 kyr the wet or decompacted sedimentation rate should be ~ 63.29 cm/kyr. Such high value is not unusual in comparable settings because much higher wet sediment accumulation rates are reported for instance, in clastic-dominated shelf areas heavily influenced by rivers (Table 1 in Gibbs, 1981), the semi-restricted Cariaco Basin (75 cm/kyr) (Spiker and Simoneit, 1982), and the East China Sea throughout the past ~ 385 kyr ($\bar{x} = 48$ cm/kyr) with peaks well over 80 cm/kyr (Sagawa et al., 2018).

7.5.6 Evidence of Regional Shallowing

Facies changes at the closing of carbon isotope segment C5 are of particular interest because this interval has been correlated with the progressive shallowing of depositional systems in the northern Iberian region (García-Mondéjar et al., 2009, 2015a, 2015b;

Millán et al., 2009, 2011; Najarro et al., 2011a, 2011b; Gaona-Narvaez et al., 2013). Shallowing is particularly evident in the Cuchía, Igaratza and Madotz sections of the Basque-Cantabrian Basin (Fig. 7-15). In the Cuchía section (Fig. 7-15), most of the deposits associated with carbon isotope segment C5 (~ 37 m to ~ 77 m) are predominately deeper-water shales grading upwards into carbonate platform deposits with orbitolinids and interbeds of siltstones and sandstones towards the end of C5 (García-Mondéjar et al., 2015a, 2015b). Sandstones with cross laminations indicative of a delta front continue into C6 (García-Mondéjar et al., 2015a, 2015b). Subsequently, siliciclastic sedimentation is replaced by limestones rich in rudists, corals, benthic foraminifera and calcareous algae (Wilmsen, 2005; Najarro et al., 2011a, 2011b; García-Mondéjar et al., 2015a, 2015b). Similarly, in the Igaratza section (Fig. 7-15), segment C5 (~ 112 m to ~ 170 m) includes essentially siltstones and marlstones coarsening upwards into interbeds of marly to sandy limestones with orbitolinids, oysters and branching corals at the close of this carbon isotope segment, and into limestones with rudists and massive corals in C6 and C7 (Millán et al., 2009, 2011). The Madotz section (Fig. 7-15), shows similar pattern as segment C5 (~ 30.5 m to ~ 40.8 m) is dominated by marlstones/claystones, which develop into grain-supported biocalcirudites dominated by orbitolinids at the onset of segment C6 with further biocalcirudites and calcarenites containing wavy contacts and fragments of non-rudist bivalves, brachiopods and echinoderms (Gaona-Narvaez et al., 2013). In summary, marine depositional settings in northern Iberia include a synchronous archive of facies change towards the end of carbon isotope segment C5 evolving into C6, not seen in contemporaneous sequences elsewhere (e.g. Heldt et al., 2008; Li et al., 2016; Aguado et al., 2014a,b). These concurrent facies

changes in the northern Iberian Peninsula are thus likely related to regional tectonic uplift rather than eustatic change in sea level.

Microfacies recorded in Unit 3 (Fig. 7-2) of the El Pujal section interpreted as changes in basin bathymetry coeval with the end of carbon isotope segment C5 suggests that the basin-wide shallowing reported for the Basque-Cantabrian Basin extended to the southeast and affected the Organyà Basin as well. Paleogeographic reconstruction of the Pyrenean realm around this time (Vacherat et al., 2017), suggests the interconnectedness of these basins via an elongated narrow (~ 200 km) sea that stretched from the proto-North Atlantic to the southeast, cutting between Iberia and Europe (Jammes et al., 2009; Vacherat et al., 2017). Here the association of progressively coarser sediments and allochems (> 50%) in Unit 3 at El Pujal (Fig. 7-2) with a decreasing trend in planktonic foraminifera (Fig. 7-3D) supports shallowing at that time. Thus, this study further illustrates how more accurate interpretations can be achieved when sedimentary indicators are combined with faunal distribution patterns.

Foraminifera are a useful bathymetric tool because the abundance of benthic taxa generally reaches a maximum on the outer shelf to upper slope, while the planktonic groups are virtually lacking in neritic environments and increasing with greater water depth (Phleger, 1951; Parker, 1954; Grimsdale and Van Morkhoven, 1955; Smith, 1955; Van Marle et al., 1987; Gibson, 1989; van der Zwaan et al., 1990). The ratio between planktonic and benthic foraminifera typically expressed as the percentage of planktonic foraminifera (%P) is thus a useful tool to infer paleodepths, although two-thirds of the variation in the %P may also be controlled by factors such as upwelling water masses and variations in salinity and turbidity (Wright, 1977). Studies of modern settings, laboratory

Figure 7-15 Comparison of the lithostratigraphic changes recorded for the end of carbon isotope segment C5 at El Pujal and various sections in the Basque Cantabrian Basin: Cuchía (García-Mondéjar et al., 2015), Igaratza (Millán et al., 2011), Madotz (Gaona-Narvaez et al., 2013).

experiments and the fossil record have also established a strong link between abundance and diversity of benthic foraminifera and oxygen content (Harman, 1964; Nolet and Corliss, 1990; Kaiho, 1994, 1999; Alve and Bernhard, 1995; Jorissen et al., 1995; den Dulk et al., 1998; Seidenkrantz et al., 2000; van Hinsbergen et al., 2005; Singh et al., 2015). These factors were taken into account in additional assessment of bathymetric changes in the El Pujal section as sedimentological and geochemical data at intervals of argillaceous limestone and marlstone beds show strong evidence of increased riverine discharge and oxygen-deficient bottom waters (Socorro and Maurrasse, 2019a,b). Therefore, these intervals were excluded in the faunal counts (van Hinsbergen et al., 2005), of the depth estimates that follow. The results show higher %P ($\bar{x} = 79\%$) for the limestones in the lowermost Unit 1, whereas the limestone beds that comprise Unit 3 show marked decrease to 18% (Fig. 7-3D). Applying the relationship between bathymetry and %P (van der Zwaan et al., 1990) the estimated average depth for Unit 1 is ~ 613 m and for Unit 3 it is ~70 m (Fig. 7-3E). These estimates thus suggest a bathymetric change of 543 m during the interval concurrent with carbon isotope segment C5 in the Organyà Basin. Despite the inherent limitations of the %P bathymetric method (e.g., restricted to thin section counts, lack of taxonomic control, fluctuation of %P with non-depth related variables, etc.), the conclusion justifies a reduction in the bathymetry of the Organyà Basin between Unit 1 and Unit 3. It further substantiates the sedimentological evidence for higher energy and shallower conditions in the Organyà Basin, similar to facies changes reported for coeval sequences in the neighboring Basque-Cantabrian Basin.

7.6 Conclusions

The present study of the uppermost 85.82 m-portion of the El Pujal section in complement with previous investigations provides a detailed sedimentological and geochemical record of the global and regional impact of the Aptian carbon cycle perturbations associated with carbon isotope segment C5 in the context of OAE1a. Salient results permit to draw the following conclusions:

1). Integration of field observations, microfacies and geochemical data allows the recognition of three distinct Units:

1a). Unit 1 (86.07 m – 114.15 m): Increases in RSTEs, P, Fe, Al, Si, and Ti occur in argillaceous limestone and marlstone beds of this interval concurrently with episodes of enhanced OM preservation and microfacies with higher pyrite concentration, reduced benthic fauna and lower degree of bioturbation. These results suggest short-lived, intermittent pulses of fluvial discharge and enhanced nutrient loads that likely fueled *in-situ* primary productivity, thus providing a source of readily mineralizable OM whose consumption led to periodic oxygen-deprived conditions. Concurrently, freshwater runoff may have led to density stratification of the water column as evidenced by recurring peaks in the gammacerane index. Unit 1 thus represents an interval of variable fluvial fluxes related to climatic fluctuations analogous to the fluctuating sedimentary facies recorded in the Mediterranean area associated with insolation-driven forcing factors during the latest Miocene and Pleistocene. Therefore, these variables explain the alternating lithology with limestones representing the least terrestrially

influenced endmember and marlstones representing points of highest terrestrial influence.

1b). Unit 2 (114.15 m – 167.96 m): Relatively higher TOC, RSTEs, P, Fe, Al, Si, and Ti occur in this marlstone-dominated interval. These higher values suggest that an increase in runoff due to established humid continental conditions prevailed in this period with quasi-permanent eutrophic surface waters and continuously established oxygen-deprived conditions. Nonetheless, a fully anoxic phase did not develop, as benthic fauna while relatively reduced are still present throughout. Freshwater discharge must have been persistent during this time as it records continually elevated gammacerane indices.

1c). Unit 3 (167.96 m – 171.89 m): Hard limestones low in TOC, P, Fe, Al, Si, and Ti, in this interval indicate the demise of previous conditions concomitant with reduction in fluvial fluxes and surface water fertility. These results are interpreted to reveal dryer climatic conditions as further suggested by an increase in smectite and a decrease in illite content. In accord, RSTEs decrease and gammacerane indices drop to near zero, signaling the termination of density stratification and renewed ventilation of the water column. Changes in microfacies, with coarser grain packstones, fewer planktonic foraminifera and increase in benthic taxa, imply a shallowing of the basin, an increase in energy conditions and a shift towards more aerobic bottom waters.

2). Molecular thermal maturity indices with average ratios consistently below equilibrium values indicate thermal immaturity. The results agree with temperatures in the range of ~ 50°C to 60°C, equivalent to the onset of the oil window.

- 3). Results from source specific biomarkers demonstrate that the OM consists of a mixture of autochthonous marine and allochthonous terrigenous sources, typical of hemipelagic settings. The relative contribution from these two end-member OM sources displays temporal variability with higher relative proportion of terrestrial OM in the argillaceous limestone and marlstone beds of Unit 1 and 2. The limestone beds that comprise Unit 3 record unusually low C_{27}/C_{29} and high TAR values, which signals to an inconclusive increasing flux of terrestrial OM. However, coeval decreases in biolimiting elements (Fe, P) suggests a decline in surface water productivity and thus reduced *in-situ* primary OM input, consequently decreasing the C_{27}/C_{29} and increasing the TAR values.
- 4). The pattern recorded by the $\delta^{13}C_{org}$ curve at El Pujal is consistent with those reported elsewhere for carbon isotope segment C5. Most importantly, the curve records a pronounced 2.76‰ negative shift, indicating the end of carbon isotope segment C5.
- 5). Based on the average duration (~ 540 kyr) calculated by other studies for carbon isotope segment C5, the calculated compacted bulk accumulation rate for this interval in the Organyà Basin equals ~ 37.13 cm/kyr. When this value is decompacted, the wet sedimentation rate equals ~ 63.29 cm/kyr, which is comparable with rates reported for shelf areas that are heavily influenced by rivers, the Cariaco Basin and the East China Sea.
- 6). Because of the continuous record and high sediment accumulation rate of the section, the generated $\delta^{13}C_{org}$ curve offers a unique detailed temporal resolution of the paleoenvironmental events recorded during carbon isotope segment C5, thus providing a refined tool for chemostratigraphic correlation.

7). Facies changes comparable to Unit 3 at El Pujal coeval with the closing of carbon isotope segment C5/base of segment C6 suggest progressive basin-wide shallowing of depositional sequences in the Basque-Cantabrian Basin, not seen elsewhere. The contrast indicates a regional shallowing of these two basins possibly related to tectonics in addition to a regional shift towards dryer climatic conditions.

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7.9 Appendices

Appendix 7A Full list of carbon geochemistry values including TIC, TOC and $\delta^{13}\text{C}_{\text{org}}$.

Sample ID	Height (m)	$\delta^{13}\text{C}$	TIC (CaCO ₃ %)	TOC (C wt%)	Sample ID	Height (m)	$\delta^{13}\text{C}$	TIC (CaCO ₃ %)	TOC (C wt%)
C-17-204	128.1	-24.09	60.39	1.28	C-17-257	171.89	-25.3	78.04	0.55
C-17-203	127.15	-24.11	60.88	1.12	C-17-256	171.16	-25	70.2	0.55
C-17-202	126.5	XXXX	61.95	1.17	C-17-255	170.49	-25.1	79.29	0.70
C-17-201	125.67	-24.24	61.19	1.29	C-17-254	169.89	-24.1	85.63	0.30
C-17-200	124.92	-24.24	61.39	1.28	C-17-253	168.87	-24	77.22	0.44
C-17-199	124.09	-24.15	59.24	1.18	C-17-252	168.36	-24.1	84.64	0.27
C-17-198	123.14	-24.25	60	1.14	C-17-251	167.96	-24	69.1	0.46
C-17-197	122.27	-24.34	58.52	1.29	C-17-250	167.61	-24	65.91	0.72
C-17-196	121.49	-24.11	59.3	1.15	C-17-249	166.81	-23.9	58.75	0.93
C-17-195	120.55	-24.11	60.19	1.07	C-17-248	166.11	-23.9	62.96	0.88
C-17-194	119.78	-24.27	59.91	1.18	C-17-247	164.61	-24	68.41	0.69
C-17-193	118.86	-24.18	62.16	1.11	C-17-246	163.26	-24.1	66.77	0.85
C-17-192	117.99	-23.99	59.33	1.19	C-17-245	162.39	-24	66.74	0.88
C-17-191	117.24	-24.17	60.82	1.26	C-17-244	161.75	-24.1	59.72	1.10
C-17-190	116.47	-24.15	62.16	1.21	C-17-243	160.98	-24.1	59.73	1.02
C-17-189	115.75	-24.16	63.33	1.04	C-17-242	160.3	-24.1	56.91	1.18
C-17-188	115.05	-24.18	62.19	1.16	C-17-241	159.58	-24.2	61.35	0.78
C-17-187	114.15	-24.12	66.13	0.74	C-17-240	158.82	-24.2	62.35	0.68
C-17-186	113.39	-24.24	64.45	0.84	C-17-239	158.02	-24.2	65.64	0.61
C-17-185	112.57	-24.14	67.38	0.67	C-17-238	157.17	-24.1	58.6	0.77
C-17-184	111.6	-24.15	67.85	0.74	C-17-237	156.42	-23.9	64.64	1.03
C-17-183	110.79	-24.1	73.15	0.64	C-17-236	155.4	-24.1	63.9	0.61
C-17-182	110.02	-24.31	71.7	0.62	C-17-235	154.34	-24.1	64.38	0.54
C-17-181	109.2	-24.23	68.21	0.90	C-17-234	153.44	-24	64.85	0.94
C-17-180	108.19	-24.26	66.02	0.90	C-17-233	152.66	-24.1	63.77	0.89
C-17-179	107.25	-24.28	66.58	0.84	C-17-232	151.99	-24.2	60.03	1.06
C-17-178	106.43	-24.43	67.02	0.84	C-17-231	151.07	-24.1	60.71	1.11
C-17-177	105.73	-24.39	70.38	0.70	C-17-230	150.21	-24.1	60.4	1.12
C-17-176	104.85	-24.43	70.38	0.70	C-17-229	149.36	-24	61	1.07
C-17-175	104.1	-24.46	68.47	0.60	C-17-228	148.33	-24.1	61.57	1.11
C-17-174	103.23	-24.51	72.39	0.77	C-17-227	147.53	-24.1	62.62	1.06
C-17-173	102.48	-24.48	68.75	0.62	C-17-226	146.61	-24.2	62.16	1.12
C-17-172	101.73	-24.49	66.50	0.76	C-17-225	145.81	-24.2	64.32	0.97
C-17-171	101.02	-24.35	62.65	1.01	C-17-224	145.04	-24.1	64.66	0.81
C-17-170	100.1	-24.59	63.12	1.24	C-17-223	144.2	-24.2	62.4	1.04
C-17-169	99.25	-24.81	63.44	0.67	C-17-222	143.45	-24.2	65.78	0.87
C-17-168	98.13	-24.73	65.52	0.75	C-17-221	142.42	-24.1	64.34	0.92
C-17-167	97.46	-24.72	63.77	0.83	C-17-220	141.62	-24.2	59.29	0.88
C-17-166	96.71	-24.87	63.68	0.87	C-17-219	140.95	-24.2	57.41	1.06
C-17-165	95.86	-24.17	70.49	0.75	C-17-218	140.25	-24.2	59.42	1.15
C-17-164	94.76	-24.46	70.03	0.83	C-17-217	139.39	-24.1	54.31	1.29
C-17-163	94.09	-24.49	71.23	0.72	C-17-216	138.46	-24.4	56.93	1.10
C-17-162	93.24	-24.63	69.68	0.73	C-17-215	137.51	-24.1	62.2	1.00
C-17-161	92.57	-24.53	70.72	0.79	C-17-214	136.49	-24.1	60.02	0.98
C-17-160	91.77	-24.48	70.13	0.64	C-17-213	135.69	-24.4	63.11	1.10
C-17-159	91.02	-24.32	63.21	0.88	C-17-212	134.74	-24.1	61.45	0.98
C-17-158	90.25	-24.20	59.58	0.75	C-17-211	133.84	-24.2	63.37	1.11
C-17-157	89.51	-24.21	56.67	1.07	C-17-210	132.8	-24.2	61.82	1.18
C-17-156	88.76	-24.36	60.53	0.83	C-17-209	132.06	-24.2	63.71	1.17
C-17-155	88.11	-24.74	68.82	0.62	C-17-208	131.29	-24.2	64.02	0.97
C-17-154	87.36	-24.67	66.40	0.73	C-17-207	130.46	-24.3	63.93	0.67
C-17-153	86.68	-24.38	68.12	0.67	C-17-206	129.71	-24.2	59.15	0.93
C-17-152	86.07	-24.64	70.21	0.79	C-17-205	128.97	-24.2	60.4	1.03

Appendix 7B Absolute values of major elements (Al, Si, Ti, Fe, P) and RSTEs (V, Ni, Co, Cr, Cu, Mo) in ppm = parts per million.

Sample ID	Height (m)	Al	Si	Ti	Fe	P	V	Ni	Co	Cr	Cu	Mo	U
C-17-257	171.89	13111	48500	638	5745	187	18.2	9.5	0.5	19.7	3.2	0.8	0.62
C-17-256	171.16	14213	57139	717	7751	188	20.6	10.7	0.8	22.2	3.8	1.1	0.72
C-17-255	170.49	7768	44985	400	6573	139	13.8	7.4	0.3	12.5	2.1	1.0	0.54
C-17-254	169.89	4610	35536	255	4299	129	9.6	8.8	0.6	13.6	1.4	0.6	0.41
C-17-253	168.87	10320	58034	506	5420	126	17.8	6.9	0.5	18.8	2.0	0.6	0.71
C-17-252	168.36	5060	41324	290	4697	122	10.2	9.5	0.4	13.5	1.5	0.7	0.46
C-17-250	167.61	21472	58509	1033	9659	188	35.2	13.0	0.4	32.6	4.2	0.6	1.07
C-17-249	166.81	28443	66649	1363	14691	467	47.0	19.4	1.5	40.2	6.3	2.4	1.19
C-17-247	164.61	22422	50901	1078	12937	253	37.7	16.9	0.7	33.3	5.3	0.9	0.88
C-17-242	160.3	27691	71937	1328	12933	273	45.7	16.8	0.8	39.9	5.9	1.1	1.36
C-17-239	158.02	22214	58733	1088	9263	163	35.7	13.3	0.4	31.0	4.8	0.7	0.83
C-17-237	156.42	24393	57903	1178	11802	242	41.6	21.4	0.9	36.0	5.1	1.5	0.99
C-17-235	154.34	24984	68339	1182	10786	336	39.4	15.4	0.7	34.2	4.7	1.9	0.91
C-17-230	150.21	28108	64012	1343	13365	268	44.0	17.0	0.8	40.2	6.0	2.0	1.04
C-17-226	146.61	27357	63764	1284	13053	255	43.2	17.3	0.9	44.9	6.9	2.2	1.27
C-17-220	141.62	29085	68059	1350	13379	310	46.4	24.1	0.9	40.5	6.5	2.2	1.07
C-17-217	139.39	31912	78404	1490	16063	367	50.8	26.6	1.6	44.3	8.2	3.3	1.07
C-17-213	135.69	26535	69706	1223	12729	295	43.7	17.1	0.9	38.6	6.1	2.4	1.00
C-17-210	132.8	26694	57477	1244	12990	199	42.5	16.3	0.8	39.7	4.8	2.0	1.08
C-17-207	130.46	25270	69278	1220	11564	321	40.0	15.0	0.7	34.8	5.1	1.8	1.03
C-17-205	128.97	27869	62496	1391	12846	226	43.2	17.4	1.0	38.6	5.7	1.4	1.09
C-17-204	128.1	27860	72488	1366	13423	334	44.5	16.1	1.1	38.4	5.6	2.2	1.13
C-17-197	122.27	28299	62893	1292	13085	312	44.5	19.5	1.1	40.5	5.8	3.0	1.06
C-17-193	118.86	27087	60477	1304	12861	289	44.6	18.6	1.0	39.6	7.2	2.4	1.05
C-17-188	115.05	26894	55669	1288	12982	207	43.0	18.2	1.0	37.0	5.5	2.6	1.11
C-17-187	114.15	26497	54648	1293	13385	185	43.7	18.4	1.0	37.5	5.0	2.1	1.24
C-17-183	110.79	20087	41349	986	11486	222	32.7	12.0	0.3	30.0	4.2	1.7	0.98
C-17-180	108.19	24973	63645	1161	11669	192	41.3	18.4	0.8	36.5	5.7	1.4	1.12
C-17-176	104.85	21062	47494	1006	12641	194	35.4	16.5	0.6	26.8	5.1	2.2	0.82
C-17-170	100.1	27071	65075	1208	13294	249	46.9	19.7	1.0	35.9	8.4	2.5	1.01
C-17-169	99.25	29918	69461	1437	12497	294	50.4	19.1	0.5	43.1	6.6	1.4	0.99
C-17-166	96.71	28392	52938	1359	12860	253	48.1	17.0	0.6	35.7	5.7	0.9	1.00
C-17-163	94.09	21773	49609	1057	9654	205	34.1	13.2	0.2	29.7	4.7	1.8	0.79
C-17-160	91.77	22752	52081	1113	10116	195	36.3	16.4	0.6	35.0	4.5	1.3	0.79
C-17-157	89.51	31876	70021	1496	15769	262	51.6	25.5	1.3	44.3	7.4	2.7	1.07
C-17-155	88.11	24935	55810	1167	11701	217	39.8	16.2	1.1	39.2	5.5	1.9	0.82
C-17-152	86.07	22380	49585	1081	9884	169	35.9	13.5	1.1	35.1	4.0	1.1	0.86
Average %RSD		1.7	2.1	5.4	12	9.4	5.7	12	14	15	18	12	17

Appendix 7C Values of all the calculated biomarker parameters.

Sample ID	Height (m)	Pr/Ph	CPI	TAR	Pr/n-C ₁₇	Ph/n-C ₁₈	Gammacerane Index	C ₂₇ /C ₂₉	Ts/(Ts+Tm)	C ₃₁ 22S/(22S+22R)	C ₂₉ 20S/(20S+20R)	C ₂₉ ββ/(ββ+αα)
C-17-257	171.89	0.97	0.95	0.84	0.29	0.27						
C-17-256	171.16	0.87	0.93	0.48	0.20	0.23	0.00	0.55	0.62	0.56	0.42	0.58
C-17-255	170.49	0.83	0.95	0.68	0.21	0.25						
C-17-254	169.89	1.25	1.02	0.41	0.33	0.27	0.01	0.57	0.63	0.54	0.54	0.65
C-17-253	168.87	0.99	0.96	0.39	0.17	0.19	0.01	0.54	0.60	0.58	0.54	0.66
C-17-252	168.36	0.89	0.98	0.44	0.15	0.17						
C-17-249	166.81	1.59	1.07	0.31	0.22	0.15						
C-17-247	164.61	1.49	1.05	0.37	0.21	0.15						
C-17-242	160.3	0.90	0.94	0.32	0.15	0.17	0.09	0.73	0.61	0.54	0.54	0.65
C-17-239	158.02	1.36	1.05	0.35	0.26	0.19						
C-17-235	154.34	1.35	1.06	0.29	0.19	0.15						
C-17-226	146.61	1.55	1.09	0.32	0.34	0.23	0.07	0.54	0.62	0.52	0.48	0.62
C-17-220	141.62	1.38	1.05	0.35	0.33	0.26						
C-17-213	135.69	1.31	1.07	0.33	0.34	0.26						
C-17-207	130.46	0.88	1.05	0.33	0.23	0.25						
C-17-204	128.1	1.26	1.05	0.32	0.30	0.24	0.09	0.49	0.63	0.59	0.42	0.60
C-17-197	122.27	1.45	1.07	0.30	0.29	0.21						
C-17-188	115.05	1.31	1.07	0.25	0.24	0.19						
C-17-183	110.79	1.04	1.05	0.29	0.22	0.20	0.04	0.93	0.58	0.56	0.57	0.60
C-17-180	108.19	1.44	1.06	0.35	0.37	0.25						
C-17-176	104.85	0.97	1.02	0.33	0.20	0.20						
C-17-170	100.1	1.54	1.04	0.41	0.50	0.34	0.09	0.58	0.63	0.48	0.55	0.64
C-17-166	96.71	1.28	1.07	0.27	0.23	0.18						
C-17-160	91.77	0.94	1.06	0.27	0.22	0.23						
C-17-157	89.51	1.23	1.06	0.30	0.28	0.24	0.09	0.55	0.62	0.55	0.59	0.62
C-17-152	86.07	1.20	1.05	0.36	0.26	0.22	0.02	0.81	0.60	0.53	0.52	0.56

8 GENERAL CONCLUSIONS

Expanded sedimentary deposits recorded in a hemipelagic setting of the Organyà Basin provided the opportunity for this comprehensive study that revealed intricate details of the marine response to perturbations of the global carbon cycle during the Aptian. To achieve the main objectives and answer the proposed questions, I employed a multi-proxy methodology integrating field observations, petrographic analyses and organic and inorganic geochemical proxies. The combined results produced the following conclusions:

- 1) Large-scale ($> 1\text{‰}$), negative, carbon isotope excursions (CIEs) that show no corresponding shifts in local sources of organic matter (OM) and are simultaneously recorded at coeval localities appear to be the result of considerable input of isotopically light carbon into the ocean/atmosphere system that affects the isotopic ratio of the global carbon reservoir. Such is the case for the globally recorded, negative intra-C2 CIE superbly registered in the expanded sedimentary record of the Organyà Basin. Variations in magnitude and duration of Lower Cretaceous massive explosive volcanism in Asia and northeast Asia SB-V (Songliao Basin) coupled with the contemporaneous emplacement of LIPs (Ontong Java) offer a plausible explanation for the observed global negative shift.
- 2) Small-scale ($< 1\text{‰}$), negative CIEs concurrent with elevated inputs of terrestrial OM are the result of regional climatic variabilities that alter riverine discharge volume and the content of terrestrially derived vegetation that contains more negative stable carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) values.

- 3) The $\delta^{13}\text{C}_{\text{org}}$ data from the sequence at El Pujal is consistent with the pattern reported elsewhere for carbon isotope segment C5 within OAE1a. The micropaleontological associations give further credence to the chemostratigraphic correlation because petrographic analysis and results from selected disaggregated samples show that hedbergellids are the most common planktonic foraminifers in this interval, accompanied by rare to common globigerinelloidids and *Leupoldina* cf. *cabri*, whose Biozone parallels the OAE1a time-interval.
- 4) Deposits of the El Pujal sequence consist of a repetitive succession of limestones, argillaceous limestones and marlstones with varying proportions of OM, carbonate and siliciclastic material. Variations in fluvial discharge linked with climatic fluctuations explain the alternating lithology with limestones representing the least terrestrially influenced end-member and marlstones representing points of highest terrestrial influence.
- 5) Surficial primary production sustained by fluvial inputs of bio-limiting nutrients provided a source of readily mineralizable OM whose consumption led to episodic oxygen-deprived conditions. Indeed, peaks in TOC along marlstone and argillaceous limestone beds, correlate well with relatively lower benthic faunal counts, lower bioturbation index, higher concentration of pyrite and enrichments in RSTEs. Concomitant spikes in gammacerane indicates a stratified water column related to pulses of freshwater outputs that may have been influential in preventing vertical mixing of oxygen depleted bottom waters with more oxygenated surface waters. Higher content of minute bivalves and gastropods in these intervals presumably flushed offshore from adjacent swamps and estuaries,

higher concentrations of lithophile elements as well as increased relative inputs of terrestrial OM, substantiates periods of intensified continental runoff.

- 6) OM preservation was not exclusively determined by redox conditions as additional aid through physical encapsulation by clay minerals likely played a significant role. In addition, coincident inputs of terrestrial OM, with more recalcitrant properties and prone to be bound to clay minerals resulting from soil forming processes, supplemented the accumulation of OM, especially during the deposition of marlstone and argillaceous limestone beds.
- 7) Molecular thermal maturity indices with average ratios consistently below equilibrium values indicate thermal immaturity. The results agree with temperatures in the range of $\sim 50^{\circ}\text{C}$ to 60°C , thus, the preserved organic geochemical data characterizes the original signals with minor to no alteration.
- 8) Data from source specific biomarkers reflects a mixed OM source, dominantly derived from bacteria, phytoplankton and aquatic macrophytes, with a relatively minor, but still significant input from terrestrial higher plants. The recorded pattern is typical of continental margins where sediments register a complex OM signal with influence from distinct, but connected ecosystems that include rivers, estuaries and the ocean system itself.
- 9) Appraisal of the aromatic lipid fraction revealed elevated concentrations of perylene coeval with increases in biomarkers indicative of allochthons OM, thus supporting its link with terrestrial vegetation input. Considering that perylene's concentration at El Pujal closely mirrors intervals of more humid climatic conditions as well as results from other studies which demonstrate its link with

wood degrading fungi, high abundance of sedimentary perylene might therefore serve as a biomarker indicating a moist continental climate in the depositional setting.

- 10) High sediment accumulation rates calculated at 37.13 cm/kyr dry and 63.29 cm/kyr wet facilitated the generation of a high-resolution $\delta^{13}\text{C}_{\text{org}}$ profile with refined details of segment C5.
- 11) The uppermost portion of the El Pujal section (Unit 3) registers the demise of previous conditions with hard limestones low in TOC, Al, Si, Ti, P and Fe, and with lower ratios of autochthonous to allochthonous OM, indicating a reduction in fluvial fluxes and surface water fertility suggesting dryer climatic conditions. At the same time, RSTEs decrease and gammacerane indices drop to near zero, signaling the termination of density stratification in the basin and renewed ventilation of the water column. Changes in microfacies, with coarser grain packstones, fewer planktonic foraminifera and increase in benthic taxa, imply a shallowing of the basin, heralding the end of OM-rich sediments in the south-central Spanish Pyrenees Basin at the end of segment C5 similar to that reported for the neighboring Basque-Cantabrian Basin.

Moreover, my dissertation has provided valuable new data applicable to the analysis of Cretaceous basins as follows:

- a) My study is the first to emphasize the globally recorded, negative intra-C2 carbon isotope excursion. The excursion has since been identified by other studies e.g., Jenkyns, 2018 “Transient cooling episodes during Cretaceous Oceanic Anoxic Events with special reference to OAE1a (Early Aptian)” attesting to the global

extent of this anomaly. Because of its common occurrence, the intra-C2 inflection is a useful chemostratigraphic marker preceding the more pronounced carbon isotope excursion of segment C3.

- b) My study is the first to analyze the sedimentological, paleontological and geochemical archive at El Pujal and determine the paleoenvironmental conditions that led to the development of its lithological expression. The results help to clarify the oceanographic, climatic and tectonic circumstances of the eastern Iberian Peninsula at this time. In addition, my investigation has contributed to the ever-increasing database of knowledge concerning the understanding of the unique depositional conditions that developed in semi-restricted basins during the Cretaceous, conditions that frequently compound to develop tremendous petroliferous potential and thus have significant economic implications.
- c) My study generated the first high-resolution $\delta^{13}\text{C}_{\text{org}}$ profile of carbon isotope segment C5 with details that are poorly recorded in more lithologically condensed sections. The detailed $\delta^{13}\text{C}_{\text{org}}$ profile combined with the applied multi-proxy methodology, further improves the understanding of transient paleoenvironmental events within OAE1, and provides a refined asset suitable for precise chemostratigraphic correlations in the absence of biostratigraphic markers.

As a corollary to this investigation, further data collection on the section will help extend the $\delta^{13}\text{C}_{\text{org}}$ profile, which due to the high sediment accumulation rates of the Basin; the sequence could conceivably serve as the “Chemotype” reference section for the OAE1a time-interval. Future research should also attempt to examine sea-surface temperatures and continental hydroclimate utilizing advanced geochemical proxies such as TEX_{86} and

stable hydrogen isotopes from epicuticular waxes of terrestrial higher plant leaves, as these data could evince a comprehensive understanding of the depositional conditions in the Organyà Basin during the Cretaceous.

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PUBLICATIONS AND PRESENTATIONS

Pending Submission - International Journal of Earth Sciences: Demise of OM-rich facies and changing paleoenvironmental conditions associated with the end of carbon isotope segment C5 of OAE1a in the north and northeastern Iberian Peninsula.

Socorro, J., Maurrasse, F.J.-M.R., 2020. Regional palaeoenvironmental influence on organic matter sequestration and characteristics of carbon isotope segment C5 in a hemipelagic sequence, Organyà Basin, northeast Spain. *The Depositional Record*. In press.

Socorro, J., Maurrasse, F.J.-M.R., 2019. Continuous accumulation of organic matter-rich sediments associated with Oceanic Anoxic Event 1a in the El Pujal section, Organyà Basin, Catalunya Spain and its relation to episodic dysoxia. *Cretac. Res.* 95, 225-251. <https://doi.org/10.1016/J.CRETRES.2018.11.009>.

Socorro, J., Maurrasse, F.J.M.R., Sanchez-Hernandez, Y., 2017. Characterization of the negative carbon isotope shift in segment C2, its global implications as a harbinger of OAE1a. *Sci. China Earth Sci.* 60, 30–43. <https://doi.org/10.1007/s11430-016-0092-5>.

“Geochemical and lithological characteristics of changing paleoenvironmental conditions associated with the end of carbon isotope segment C5 of OAE 1a in the south-central Spanish Pyrenees.” Jander Socorro, Florentin J-M.R. Maurrasse. GSA 2019 September 22-25, Arizona, USA.

"Geochemical and microfacies implication of the El Pujal section at the close of carbon isotope segment C5: Organyà Basin, Catalunya, Spain." Jander Socorro, Florentin J-M.R. Maurrasse. AAPG 2019 May 19-22, Texas, USA.

"Regional fluctuating environmental conditions and shallowing event in the north and northeastern Iberian Peninsula during the end of carbon isotope segment C5: Organyà Basin, Catalunya, Spain." Jander Socorro, Florentin J-M.R. Maurrasse. GSA 2018 November 4-7, Indiana, USA.

"Regional paleoenvironmental influence on OM sequestration and carbon isotope segment C5 in the hemipelagic sequence at the EL Pujal Section, Organyà Basin, northeast Spain." Jander Socorro, Florentin J-M.R. Maurrasse. AAPG 2018 May 20-23, Utah, USA.

"Local expression of global forcing factors in Lower Cretaceous, Aptian carbon isotope segment C5: El Pujal section, Organyà Basin, Catalunya Spain." Jander Socorro, Florentin J-M.R. Maurrasse. AGU 2017 December 11-15, Louisiana, USA.

"Geochemical characterization of the basal El Pujal section, Organyà Basin (NE Spain), in relation to its chronostratigraphic position to OAE1a." Jander Socorro, Florentin J-M.R. Maurrasse. 10th ISC International Symposium on the Cretaceous 2017 August 21-26, Vienna, Austria.

"Trace elements and biomarker results of the El Pujal section, Organyà Basin, Catalunya, NE Spain, in relation to OAE1a." Jander Socorro, Florentin J-M.R. Maurrasse. AGU 2016 December 12-16, California, USA.

"Continuous episodic dysoxia related to OAE1a, Organyà Basin, El Pujal section, Catalunya, NE Spain." Jander Socorro, Florentin J-M.R. Maurrasse. GSA 2016 September 25-28, Colorado, USA.

"Characterization of the negative carbon isotope shift in segment C2 of the Organyà Basin, El Pui section, Spain; A potentially useful chemostratigraphic marker prior to OM-rich interval associated with Oceanic Anoxic Event 1a (OAE 1a)." Jander Socorro, Florentin J-M.R. Maurrasse, Yosmel Sanchez-Hernandez. AAPG 2016 September 6-9, Cancun, Mexico.

"Biomarker characterization of the negative carbon isotope shift in segment C2 of the El Pui section, Organyà Basin, Catalunya, Spain." Jander Socorro, Florentin J-M.R. Maurrasse, Yosmel Sanchez-Hernandez. IGCP 609 Workshop September 5-11, 2015. Nanjing, China.